PB86-156593

In-Use Evaporative Canister Evaluation

Southwest Research Inst., San Antonio, TX

Prepared for

Environmental Protection Agency, Ann Arbor, MI

Dec 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-156593

United States
Environmental Protection
Agency

Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA 460/3-85-003
December 1985

Air

EPA

In-Use Evaporative Canister Evaluation

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA 460-3-85-003	2.	3. RECIPIENT'S ACCESSION NO. PB86 156593
4. TITLE AND SUBTITLE In-Use Evaporative Canister Evaluation		5. REPORT DATE September 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Mary Ann Warner-Selph		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute Department of Emissions Research 6220 Culebra Road San Antonio, Texas 78284		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-03-3162
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Protection Agency 2565 Plymouth Road Ann Arbor, Michigan 48105		13. TYPE OF REPORT AND PERIOD COVERED Final (Dec. 1984 - July 1985)
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This program involved the evaluation of 24 samples of charcoal from in-use evaporative canisters. The Environmental Protection Agency (EPA) provided the canisters from programs conducted by the EPA, Tennessee Valley Authority (TVA), and Southwest Research Institute (SwRI) on both alcohol blend-fueled and unleaded gasoline-fueled vehicles. Ten canisters from alcohol blend-fueled vehicles, eight from gasoline-fueled vehicles, and six from vehciles with unknown fuel histories were tested.

A system was developed to remove and collect the effluent from samples of canister charcoal at room temperature (cold purge) and under heated conditions (hot purge). Charcoal samples of about 50 g were first cold purged with dry nitrogen at a flowrate of approximately 1.5 cfm. Butane working capacity was then measured, and the charcoal was subsequently hot purged at approximately 355-375°F (180-190°C). The effluent was sampled during selected cold and hot purge cycles and analyzed for water content, methanol, ethanol, tertiary butyl alcohol (TBA), total hydrocarbons (THC), and selected detailed hydrocarbons.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Evaporative Canisters Methanol Charcoal Evaluation	

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 105
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE $16.95

EPA Form 2220-1 (9-73)

EPA 460/3-85-003

In-Use Evaporative Canister Evaluation

by

Mary Ann Warner-Selph

Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

Contract No. 68-03-3162
Work Assignment 27

EPA Project Officer: Craig A. Harvey

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

December 1985

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Office, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan 48105.

This report was furnished to the Environmental Protection Agency by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, in partial fulfillment of Contract No. 68-03-3162. The contents of this report are reproduced herein as received from Southwest Research Institute. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA 460/3-85-003

FOREWORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The work was performed between December 1984 and July 1985 under EPA Contract No. 68-03-3162, Work Assignment 27. It was identified within Southwest Research Institute as Project 03-7338-027. The EPA Project Officer was Craig A. Harvey of the Office of Mobile Source Air Pollution Control, Emission Control Technology Division, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan. The Southwest Research Institute Project Manager was Charles T. Hare, and the Project Leader was Mary Ann Warner-Selph.

ABSTRACT

This program involved the evaluation of 24 samples of charcoal from in-use evaporative canisters. The Environmental Protection Agency (EPA) provided the canisters from programs conducted by the EPA, Tennessee Valley Authority (TVA), and Southwest Research Institute (SwRI) on both alcohol blend-fueled and unleaded gasoline-fueled vehicles. Ten canisters from alcohol blend-fueled vehicles, eight from gasoline-fueled vehicles, and six from vehicles with unknown fuel histories were tested.

A system was developed to remove and collect the effluent from samples of canister charcoal at room temperature (cold purge) and under heated conditions (hot purge). Charcoal samples of about 50 g were first cold purged with dry nitrogen at a flowrate of approximately 1.5 cfm. Butane working capacity was then measured, and the charcoal was subsequently hot purged at approximately 355-375°F (180-190°C). The effluent was sampled during selected cold and hot purge cycles and analyzed for water content, methanol, ethanol, tertiary butyl alcohol (TBA), total hydrocarbons (THC), and selected detailed hydrocarbons.

TABLE OF CONTENTS

		Page
FOREWORD		iii
ABSTRACT		iv
LIST OF FIGURES		vii
LIST OF TABLES		viii
I.	INTRODUCTION	1
II.	PROCEDURES AND INSTRUMENTATION	3
	A. Handling and Storage of Charcoal Canisters	3
	B. Sampling System	5
	C. Working Capacity	9
	D. Analytical Procedures	9
III.	DEVELOPMENT AND VALIDATION OF SAMPLING SYSTEM	13
	A. Development of Sampling System	13
	B. Practice Cold and Hot Purge Cycles and Working Capacity Measurement of an In-Use Charcoal Sample	14
	C. Validation of the Charcoal Sampling System	17
	D. Water Content of New Unused Charcoal	19
	E. Surface Area of Unused Charcoal Samples	20
IV.	RESULTS	21
	A. Water Content	21
	B. Methanol, Ethanol, and TBA	27
	C. Total Hydrocarbons	29
	D. Comparison of Charcoal Weight Loss to the Sum of Water Content, Alcohols, and Total Hydrocarbons	29
	E. Working Capacity	31
	F. Detailed Selected Hydrocarbons	31
	G. Summary of Results	40
V.	QUALITY ASSURANCE	43
REFERENCES		45

TABLE OF CONTENTS (CONT'D)

APPENDICES

A. BUTANE WORKING CAPACITY PROCEDURE
B. THE MEASUREMENT OF METHANOL, ETHANOL, AND TERTIARY BUTYL ALCOHOL IN EXHAUST
C. CALCULATION OF HYDROCARBON RECOVERY (IN GRAMS) FROM BAG PPMC
D. CHARCOAL WEIGHT LOSS AND CONTINUOUS HC LEVELS DURING THE PURGE CYCLE (OF DELCO IN-USE CHARCOAL) OF THE BUTANE WORKING CAPACITY PROCEDURE
E. WORKING CAPACITY FOR INDIVIDUAL WORKING CAPACITY CYCLES
F. SELECTED DETAILED HYDROCARBONS

LIST OF FIGURES

Figure		Page
1	Metal Charcoal Holder	6
2	Schematic of Charcoal Purge and Sampling System	7
3	Charcoal Purge and Sampling System	8
4	Selected Detailed Hydrocarbon Chromatogram for Canister Number EPA 1480049 Hot Purge Cycle, Diluted 1 to 10	32
5	Comparison of the Distribution of Detailed Hydrocarbon Emissions from Hot Purge Cycles Averaged by Fleet and by Fuel Type	37
6	Comparison of the Distribution of Detailed Hydrocarbon Emissions Sampled from TVA Charcoal Samples During Cold and Hot Purge Cycles	38

LIST OF TABLES

Table		Page
1	Evaporative Charcoal Canisters Evaluated	4
2	Continuous HC Concentrations and Rate of Charcoal Weight Loss of In-Use Delco Charcoal During Cold and Hot Purge Cycles	15
3	Breakthrough Time of Charcoal Using Butane	16
4	Butane Working Capacity of In-Use Delco Charcoal	17
5	Recoveries of Gasoline, Methanol, Ethanol, TBA, and Water from New Delco and Motorcraft Charcoals	18
6	Water Content of Unused Charcoal	19
7	Summary of Results of In-Use Evaporative Canister Charcoal Testing on 50 g Samples of Charcoal	22
8	Comparison of Charcoal Hot Purge Cycle Emissions and Working Capacity by Fleet and Vehicle Fuel Type for 50 g Samples of Charcoal	23
9	Comparison of Charcoal Hot Purge Emissions and Working Capacity by Vehicle Class and Fuel Type for 50 g Samples of Charcoal	24
10	Comparison of Cold Purge Cycle and Hot Purge Cycle TVA Charcoal Sample Emissions for 50 g Samples of Charcoal	25
11	Comparison of Charcoal Weight Loss to the Sum of Water Content, Alcohols, and Total Hydrocarbons	26
12	Compound Numbers for Selected Detailed Hydrocarbons	34
13	Percentage of Each Hydrocarbon Group to Total Detailed Hydrocarbons	35
14	Percentage of each Hydrocarbon Group to Total Detailed Hydrocarbons from Cold and Hot Putge Cycles of TVA Charcoals	39
15	Summary of Percentages of Paraffins, Olefins and Aromatics in Purged Charcoal Effluent from 50 g Samples from In-Use Evaporatove Canisters	40
16	Precision, Accuracy, and Completeness	43

I. INTRODUCTION

The effect of alcohol blends and related co-solvents on evaporative emissions has been studied in several programs at SwRI. One project involved the measurement of evaporative emissions during the Sealed Housing for Evaporative Determinations (SHED) test on vehicles fueled with an alcohol blend and on vehicles fueled with unleaded Indolene. Another project involved the laboratory evaluation of reduced-sized charcoal canisters that had been exposed to a hydrocarbon blend and a simulated alcohol blend. The work described in this report, which involves the analysis of the effluent from in-use evaporative canister charcoal, is part of the ongoing research effort to quantitate the effect of methanol, ethanol, and TBA on charcoal canisters. The purpose of this work was to determine any differences in the quantity of specific compounds adsorbed on evaporative canister charcoal from gasoline/alcohol blend fueled vehicles as compared to those from gasoline fueled vehicles. To relate any such differences to performance of the charcoal, butane working capacity tests were also conducted on each charcoal sample.

The first task of the program involved the design and development of a system to remove and sample the compounds retained by in-use canister charcoal. A sample pump was used to draw dry nitrogen through the charcoal sample to purge off hydrocarbons, alcohol, and water. Purging was done at room temperature (cold purge) and then at approximately 355-375°F (180-190°C, hot purge). The charcoal effluent was sampled for methanol, ethanol, TBA, water, THC, and selected detailed hydrocarbons during all hot purges and during six cold purge cycles. Purging was separated into cold and hot purges to determine how much of the adsorbed material would desorb easily versus how much would tend to remain on the charcoal despite room temperature purging.

Three butane working capacity tests were performed on the charcoal after cold purging and before heated purging. This involved loading butane onto the charcoal until a hydrocarbon breakthrough level of 1000 ppmC was reached, after which the charcoal was cold purged. The charcoal canister was weighed after butane loading and after purging; the difference in the two weights is defined as the working capacity. THC and detailed hydrocarbons were measured on selected cold purges during working capacity tests.

The second task of this project involved the evaluation of 24 evaporative canister charcoal samples. The charcoal was removed from the canisters as needed and stored in capped glass bottles. The charcoal was shaken in the bottle to provide a uniform sample and then approximately 50 g was removed and placed in a reduced-sized metal canister for testing. Ten charcoal samples were from vehicles which had been operated with alcohol blends, eight samples were from vehicles that had been operated with unleaded gasoline, and six were from vehicles with an unknown fuel history. The charcoal samples were subjected to three procedures:

- Room temperature (cold) purge with nitrogen until charcoal weight loss is less than 1 g/hr.

- Butane working capacity
  - Load charcoal with butane to 1000 ppmC breakthrough level
  - Cold purge to weight loss of less than 1 g/hr
  - Weigh before and after cold purge; difference is working capacity
  - Repeat two times
- Hot purge at ~355-375°F (~180-190°C) with nitrogen until charcoal weight loss is less than 1 g/hr.

Methanol, ethanol, TBA, water content, THC, and detailed hydrocarbons were measured during both cold and hot purge cycles for six of the 24 charcoal samples. THC and detailed hydrocarbons were also measured during the cold purge cycle of the working capacity procedure for the same six charcoal samples. The effluent from the remaining charcoal samples was analyzed for alcohols, water content, THC, and detailed hydrocarbons during the hot purge only. For these samples, no analyses were performed during the cold purge cycle of the working capacity procedure.

II. PROCEDURES AND INSTRUMENTATION

The procedures and instrumentation required to sample and analyze alcohols, water, and hydrocarbons from in-use evaporative charcoal samples are described in this section. The handling and storage of the evaporative test canisters is also described. The sampling system was designed to remove compounds retained on charcoal in a stream of nitrogen. Impingers were used to sample alcohols, Drierite to sample water, and Tedlar bags for hydrocarbons. Gas chromatography was used to analyze alcohols and hydrocarbons, and water content was measured by Drierite weight gain. Butane working capacity of the charcoal was also measured.

A. Handling and Storage of Charcoal Canisters

Eighteen canisters were shipped to SwRI from the TVA and nine from the EPA, Ann Arbor. Fourteen canisters were supplied by the EPA to the Department of Emissions Research, SwRI under Contract Number 68-03-3192, Work Assignment Number 7, using vehicles that had accumulated mileage under a DOE program. Twenty-four of these 41 canisters were selected for testing, and they are described in Table 1.

The selection of the canisters was based on acquiring charcoal data by groups of similar vehicle types. Higher priorities were assigned to multiple canisters from the same engine family. The Work Plan originally called for the analysis of 34 canisters. The number was reduced to accommodate an increased level of work effort. This increased level of work included the addition of a working capacity cycle and a recovery test on the sampling system.

The canisters from the TVA and EPA were received with tape covering the port openings, while the canisters from SwRI were provided with stoppers inserted into the port openings. The canisters were stored at room temperature prior to testing.

The TVA blend fueled vehicles had been operated for one year, alternating in six week periods with the blend and with unleaded gasoline. Following this was six months' operation with gasoline before the canisters were removed for this test program. The TVA gasoline/alcohol blend fuel was a tailored blend with a distillation curve very similar to the gasoline and a slightly lower RVP (e.g. 9.95 psi blend, 10.7 psi gasoline in the summer).

The SwRI (DOE fleet) blend was a splash blend with the base gasoline, and therefore had a much higher RVP (about 12 vs. 9 psi). These vehicles had been operated since new (about 14,000 miles) on their respective mileage accumulation fuels except for (a) one SHED test at about 10,000 miles using a matched volatility version of the blend in all the vehicles, and (b) a number of SHED tests with an 11.5 RVP gasoline at the end of the mileage accumulation. The EPA canisters were from in-use vehicles, so their fueling histories are unknown.

TABLE 1. EVAPORATIVE CHARCOAL CANISTERS EVALUATED

Source	Canister Number	Vehicle Description	Vehicle Fuel Type	Total Charcoal Weight, g
TVA	2090[a]	82 Chevy Chevette 98 CID	Gasoline	543.4
	2099[a]	82 Chevy Chevette 98 CID	Gasoline	546.3
	1925	81 Chevy Chevette 98 CID	Gasoline	583.3
	8887[a]	81 Ford Fairmont Wagon 140 CID	Gasoline	487.3
	1991[a]	82 Chevy Chevette 98 CID	Gasoline-Alcohol Blend[b]	567.3
	2067[a]	82 Chevy Chevette 98 CID	Gasoline-Alcohol Blend[b]	567.3
	1725	81 Chevy Chevette 98 CID	Gasoline-Alcohol Blend[b]	567.2
	1747	81 Chevy Chevette 98 CID	Gasoline-Alcohol Blend[b]	581.4
	8961[a]	81 Ford Fairmont Wagon 140 CID	Gasoline-Alcohol Blend[b]	520.9
	8902	81 Ford Fairmont Wagon 140 CID	Gasoline-Alcohol Blend[b]	460.9
SwRI (from DOE fleet)	201	84 Ford Escort 98 CID	Gasoline	523.2
	202	84 Ford Escort 98 CID	Gasoline	539.9
	205	84 Ford Escort 98 CID	Gasoline	541.3
	206	84 Ford Escort 98 CID	Gasoline	500.6
	101	84 Ford Escort 98 CID	Gasoline-Alcohol Blend[c]	533.5
	102	84 Ford Escort 98 CID	Gasoline-Alcohol Blend[c]	541.1
	104	84 Ford Escort 98 CID	Gasoline-Alcohol Blend[c]	528.1
	106	84 Ford Escort 98 CID	Gasoline-Alcohol Blend[c]	542.7
EPA	A1480008	83 Ford DFM3.3V1GXFX[d]	e	459.2
	A1480049	83 Ford DFM3.3V1GXFX[d]	e	550.0
	A1480073	83 Ford DFM3.3V1GXFX[d]	e	513.8
	A1480039	83 Ford DFM3.3V1GXFX[d]	e	439.5
	A1480060	83 Ford DFM3.3V1GEF6[d]	e	489.1
	A1480096	83 Ford DFM3.3V1GEF6[d]	Gasoline and Oxinol 50[f]	539.1

---

[a] Additional analyses during cold purge and working capacity cycles
[b] 5% O_2 gasoline-alcohol blend
[c] 4% (vol) methanol, 2% (vol) ethanol, 2% (vol) TBA
[d] Engine family number
[e] Unknown
[f] Unknown, but vehicle was tested (FTP) once with Oxinol 50 prior to canister removal

B. Sampling System

The charcoal from each test canister was removed and placed in a glass jar. The jar was shaken to mix the charcoal and to provide a representative sample for testing. Fifty grams of charcoal was transferred to a metal container that was screened on the bottom to secure the charcoal. A Swagelok fitting had been welded to the top of the container to allow nitrogen flow through the charcoal. Views of the canister are shown in Figure 1. Glass wool was also placed on the screen and at the fitting to minimize the loss of fine charcoal particles.

The system, which was designed to draw nitrogen through the charcoal, consisted of two chambers; one for room-temperature and one for heated purging. A schematic of the sampling system is shown in Figure 2, and views of the system are shown in Figure 3. Gaseous nitrogen from a liquid nitrogen cylinder was directed to a Boekel desiccator adapted to gas flow for cold (room temperature) purging, or to a Blue M oven adapted to gas flow for hot purging.

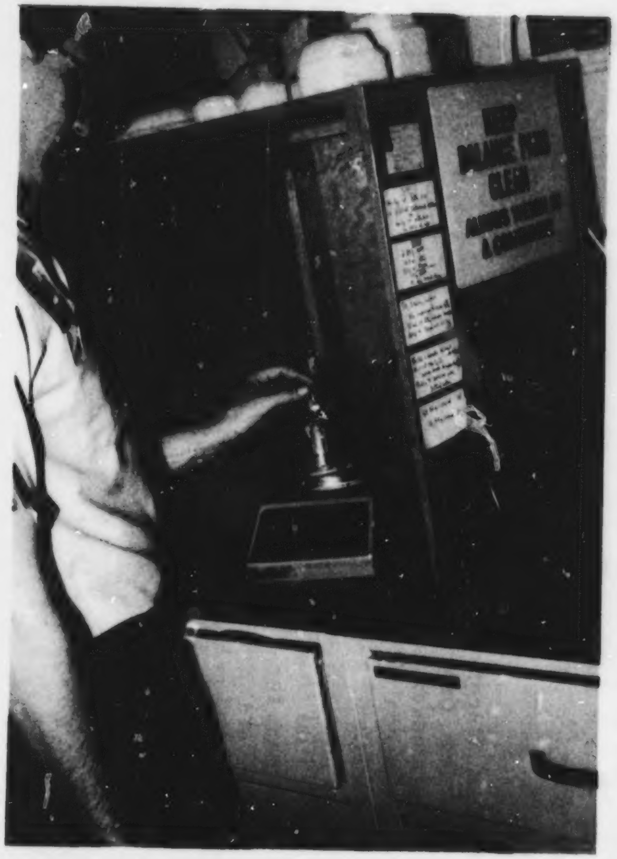
The heated purge system was also equipped with a sleeve heater on the inlet line to the oven. Excess nitrogen flow was used to create a slight positive pressure in the system with the pump "on". This reduced the possibility of room air being drawn into the purge system.

A Thomas dual-head pump, operating at approximately 42 ℓ/min (1.5 cfm), directed sample flow to a four-way manifold with a vent to the atmosphere for excess flow. Four smaller Thomas pumps withdrew samples of charcoal effluent from the manifold for alcohol, water content, bag hydrocarbon, and continuous hydrocarbon analyses. Alcohols were sampled in impingers and water in a Drierite tube at sample flowrates of about 4 ℓ/min; and bag hydrocarbons were collected at approximately 4 ℓ/min during working capacity purges, and at approximately 1 ℓ/min during other purge cycles. A continuous hydrocarbon analyzer, Beckman Model 400, was operated according to the manufacturer's specifications to monitor the sample stream for hydrocarbons.

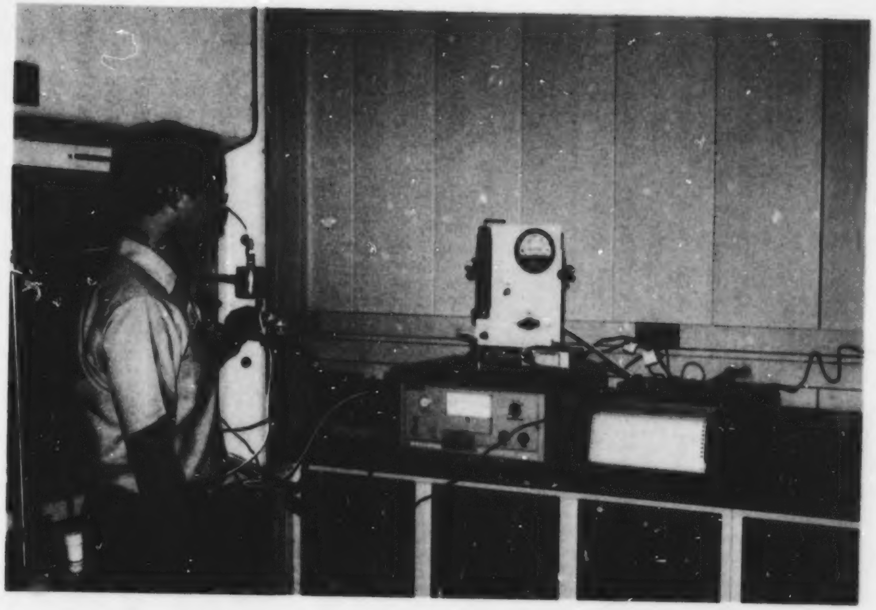
The charcoal sample was cold or hot purged until the rate of charcoal weight loss was less than 1 g/hr. A large portion of the weight loss is attributable to removal of hydrocarbons, and thus the concentration of hydrocarbons in charcoal effluent provides a good indication of weight loss. A continuous hydrocarbon level of 300 ppmC was experimentally found to correspond with a charcoal weight loss of less than 1 g/hr (the calculated value was 0.4 g/hr)[a]. Initial charcoal purges were performed to a hydrocarbon level of 300 ppmC, however, the time required to purge to 300 ppmC was in excess of 1 1/2 hours. Therefore, a 600 ppmC hydrocarbon cut-off level was chosen for sample purging. A 600 ppmC hydrocarbon level is equivalent to an emission rate of 0.9 g/hr of hydrocarbons, still less than the maximum desired rate of 1 g/hr. Using the 600 ppmC cut-off level reduced the length of each purge cycle to less than 1 1/2 hours for most charcoal samples.

---

[a] $(300\ \text{ppmC}/10^6) \times (\text{purge rate, } 1.5\ \text{cfm}) \times (60\ \text{min/hr}) \times (16.33\ \text{g/ft}^3\ \text{HC})$
$= 0.4\ \text{g/hr}$



Weighing Charcoal Holder



Measuring Butane Breakthrough

Figure 1. Metal charcoal holder

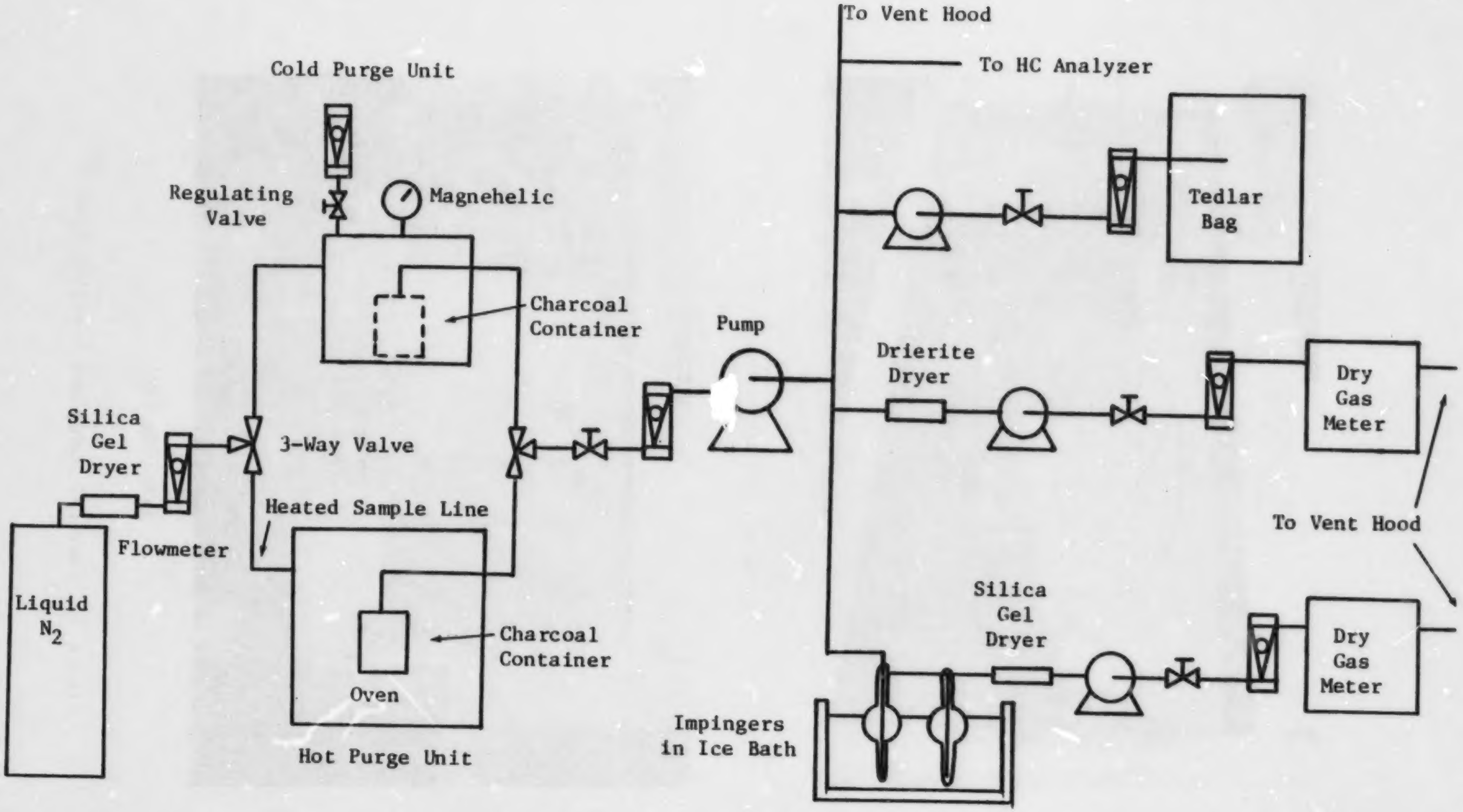
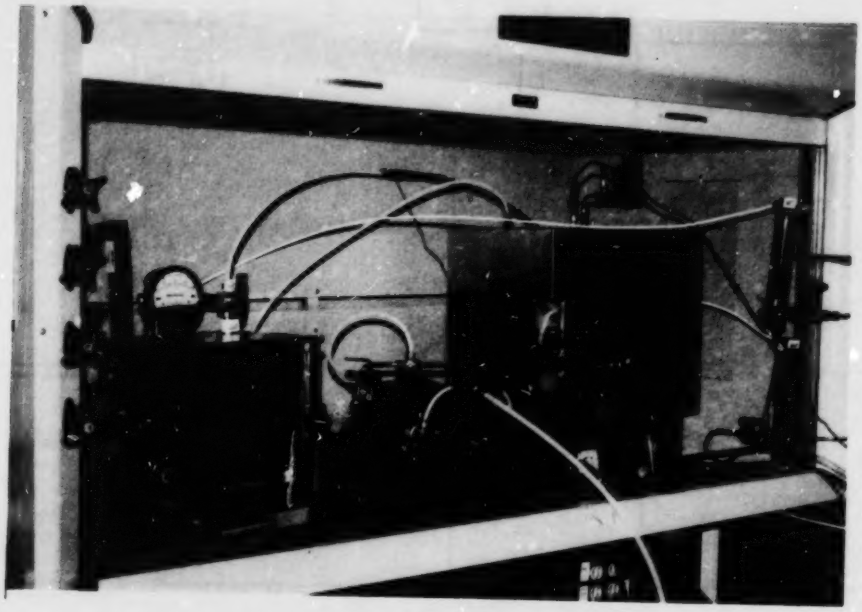
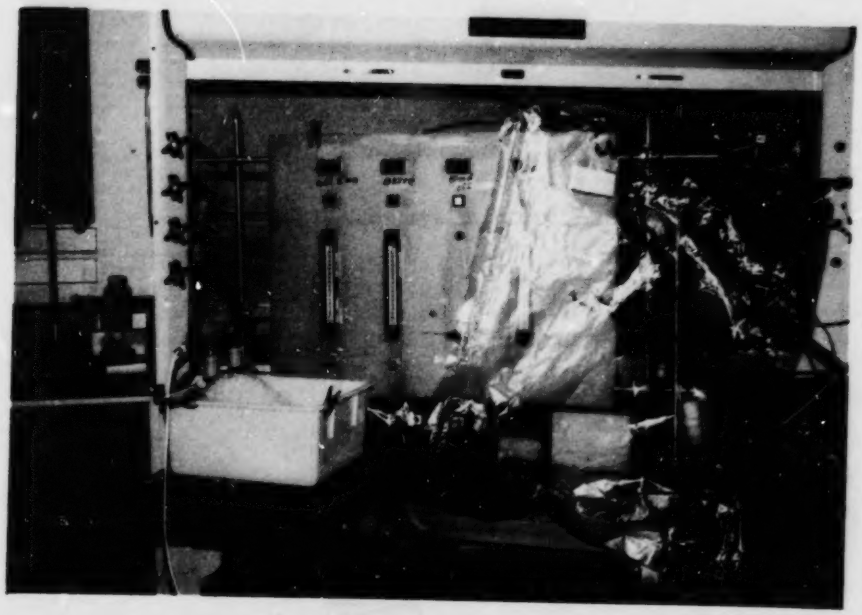

Cold Purge Unit
Regulating Valve
Magnehelic
Charcoal Container
Silica Gel Dryer
3-Way Valve
Heated Sample Line
Flowmeter
Liquid N_2
Charcoal Container
Oven
Hot Purge Unit
Pump
To Vent Hood
To HC Analyzer
Tedlar Bag
Drierite Dryer
Dry Gas Meter
To Vent Hood
Silica Gel Dryer
Dry Gas Meter
Impingers in Ice Bath

Figure 2. Schematic of charcoal purge and sampling system



Cold and Hot Purge Units



Sampling Cart

Figure 3. Charcoal purge and sampling system

C. Working Capacity

The working capacity of each charcoal sample was measured after the cold purge cycle according to a butane working capacity procedure provided by the EPA Project Officer. The procedure is found in Appendix A. Working capacity is defined as the difference between the charcoal weight when loaded with butane (at about 280 mℓ/min to 1000 ppmC breakthrough level) and the charcoal weight after cold purging the charcoal to 600 ppmC. Measurement of working capacity was included in the program at the request of the Project Officer to provide additional charcoal information. The total number of charcoal samples originally to be analyzed was reduced to accommodate the added level of effort.

Butane working capacity is a measure of the charcoal's ability to "hold" onto butane while loading at 280 mℓ/min and then to release it during a cold purge cycle. The charcoal samples typically lost the same amount of weight from purging as was added during butane loading. Thus, the difference between working capacities was in the butane loading cycles. Some charcoals were able to retain butane to a greater degree at the chosen flowrate before butane vapors "broke through" the charcoal at a measured concentration of 1000 ppmC.

D. Analytical Procedures

Charcoal effluent samples were analyzed by several procedures. Impinger samples were analyzed for methanol, ethanol, and TBA. A Drierite tube was weighed before and after testing to determine water content and bag samples were analyzed for THC and detailed individual hydrocarbons. The procedures are described in this section.

1. The Measurement of Methanol, Ethanol, and TBA

Methanol, ethanol, and TBA were sampled by bubbling the charcoal effluent during a cold or hot purge cycle through two glass impingers in series, each containing 25 mℓ of deionized water. The temperature of the impingers was maintained at 0-5°C by an ice bath, and the flow rate through the impingers was maintained at 4 ℓ/min by a sample pump. The impinger alcohol samples were transferred to polyethylene containers after completion of a cold or hot purge cycle.

The alcohol samples were analyzed on a Perkin-Elmer 3920B gas chromatograph (GC) equipped with a flame ionization detector. A 5 μℓ portion of the sample is injected into the GC and analyzed isothermally at 221°F (105°C) for methanol, at 284°F (140°C) for ethanol, and at 302°F (150°C) for TBA. Sample peak areas are compared to external standards to obtain alcohol concentrations in $\mu g/m^3$. These values are converted to mg of methanol, ethanol, or TBA using the following equation:

$$\mu g/m^3 \times \text{Purge Flowrate, ft}^3/\text{min} \times \text{Purge Length, min.} \times 0.028317\ m^3/ft^3 \times 10^{-3}\ mg/\mu g = \text{mg alcohol}$$

A more detailed version of this procedure is found in Appendix B.

2. The Measurement of Water Content

Water is sampled from the charcoal effluent during the cold or hot purge cycle using a preweighed 4 inch polyethylene drying tube filled with Drierite. The tube is weighed after the purge cycle to determine water weight gain to 0.01 g. Water content of the charcoal sample is calculated using the following equations:

Equation 1:

$$\text{Purge Flow Volume, ft}^3 = \text{Purge Flowrate, ft}^3\text{/min} \times \text{Purge Length, min}$$

Equation 2:

$$\text{Drierite Flow Volume} = \text{Measured Flow Through Drierite Tube, ft}^3 \times \frac{\text{Bar. Press., in Hg}}{\text{29.92 in Hg}} \times \frac{528^{\circ}\text{F}}{\text{Temp }^{\circ}\text{F} + 460}$$

$$\text{Charcoal Sample Water Content, g} = \text{Drierite Wt. Gain, g} \times \frac{\text{Equation 1}}{\text{Equation 2}}$$

A test was performed with the dryer tube to determine if Drierite absorbs alcohol in addition to water. One milliliter of methanol was evaporated into a stream of dry nitrogen. The methanol vapor was pumped through a Drierite tube until the methanol was fully evaporated. The drying tube was weighed before and after the test and was found not to have gained weight, so methanol was apparently not absorbed onto the Drierite. A water-methanol sample was not tested to determine the affinity of moist Drierite for methanol. However, for all but one sample, the weight of methanol in charcoal effluent was less than or equal to 5 percent of the weight of the measured water.

3. The Measurement of THC

The procedure used for the measurement of bagged total hydrocarbons (THC) is similar to that listed in the Code of Federal Regulations.(1)* THC's were measured using a heated FID. The procedure included the use of calibration gases for sample quantification. No corrections were made for the presence of alcohol.

4. The Measurement of Detailed Individual Hydrocarbons

Detailed hydrocarbons were analyzed on a bag sample collected at approximately 1 ℓ/min during the cold or hot purge cycle or on a bag sample collected at 4 ℓ/min during the working capacity purge cycle (the same sample was also used for THC analysis). A gas chromatographic system was used to analyze the bag samples. It permits the quantitative determination of more than 80 of the hydrocarbons in charcoal effluent, carbon numbers 4 to 10. The capillary column used to separate these compounds is a Perkin-Elmer F-50 versilube, 150 ft x 0.020 inch WCOT stainless steel column. The column is initially cooled to -139°F (-95°C) for sample injection. Upon injection, the temperature is programmed at a 7°F (4°C) increase per minute to 185°F (85°C). The column temperature is held at 185°F for approximately 15 minutes to permit complete column flushing. A flow controller is used to maintain a 1.5 mℓ/min carrier flow rate. The 10 mℓ sample volume for C_4-C_{10} permits accurate determination of 0.1 ppm C with the flame ionization detector used (Perkin-Elmer 3920B). The baseline is re-established at about 60 minutes after injection, resulting in about 1 1/2 hours of analytical turn-around time.

---

*Numbers in parentheses designate references at the end of this report.

Calibration of the gas chromatograph is achieved using a benzene standard traceable to a NBS benzene standard. The per unit response of the FID for each individual HC component is assumed to be equivalent for calculations. This assumption was based on a study reported in Basic Gas Chromatography by McNair and Bonelli which reported relative FID sensitivities of over 30 paraffin, olefin, and aromatic compounds. The FID sensitivity responses of the compounds varied 15 percent from maximum to minimum, while the majority of the responses (>94 percent) varied only 10 percent. The proportional amount of each compound was calculated based on the ratio of individual peak areas to total peak area.

Gaseous hydrocarbon samples for detailed speciation were collected in Tedlar bags. Several experiments have been conducted at EPA-RTP to examine bag wall losses and stability of the sample mixture. Gasoline samples were prepared with air in forty (40)-liter bags and analyzed over a twelve-hour time interval. Exhaust samples were also analyzed over a twelve-hour interval. The overnight (12-hour) loss observed was 5% of the gasoline samples, and 10% of the exhaust samples. The bag stability was considered adequate for samples analyzed within eight hours of collection.(2)

III. DEVELOPMENT AND VALIDATION OF SAMPLING SYSTEM

The development of the sampling system and the associated operating procedures involved several steps. First, the design of the sampling system went through several alterations until it could properly handle in-use evaporative charcoal samples. After the sampling system was completed, a practice run on in-use charcoal was performed to further define operating parameters. In the third step, alcohol, water, and hydrocarbon recovery experiments were conducted with spiked new charcoal samples to validate the operation of the sampling system. Fourth, new, unused charcoal samples were cold and hot purged and the water content determined. For additional information, the surface areas of unused Delco and Motorcraft charcoals were measured using the Brunauer, Emmett, and Teller Method (B.E.T.) for surface area analysis.

A. Development of Sampling System

The initial intent of the program was to test the charcoal from full-size evaporative canisters, however, a preliminary test using the entire charcoal contents of an in-use 1980 Mercury Cougar canister indicated a downsized system would provide a better method for sampling charcoal effluent. The charcoal, which weighed 476.2 g, was transferred to a metal container. It was subjected to one 20-minute cold purge, two 20-minute hot purges, and a shortened 13-minute hot purge. The system became saturated with liquid fuel which had condensed in the flowmeters, valves, pumps, dryer tubes, and Teflon lines during the final hot purge. Before the final cycle, the oven temperature had been elevated and allowed to stabilize with the canister inside the oven. Apparently fuel evaporated from the canister during the warm-up period and produced a slug of liquid fuel when purging began. Excessive hydrocarbons were also produced during the cold and first two hot purge cycles, even without liquid fuel present. Hydrocarbon levels above 10,000 ppmC, the upper limit of the detector, were measured in all purge cycles.

Due to the inability of the sampling system to handle the amount of charcoal effluent produced from the standard size canister tested, the system had to be expanded and/or the amount of charcoal sample reduced. A larger purge pump was employed to provide additional dilution of charcoal effluent, and the amount of charcoal used for testing was reduced to approximately one tenth of the charcoal in a standard size canister. The larger pump flowed at about 42 ℓ/min (the original pump flowed at 18 ℓ/min), providing additional dilution of (42 / 18) x 10 ≈ 23 times. The water sampling system was also scaled down with a smaller, lighter weight sampling tube used to trap water from the smaller charcoal sample. The lighter tube could be weighed to 0.01 g, whereas the original water sampling tube could be weighed to only 0.1 g. The methanol, ethanol, and TBA analytical procedure was still sufficiently sensitive to the alcohols at the reduced levels.

In addition to downsizing the sampling system, the problem of moist room air leaking into the system during purging and in the weighing process had to be addressed. The relatively high humidity level of room air would cause errors in measuring the water content of charcoal. Excess nitrogen was therefore

Preceding page blank

directed to the sample chambers to minimize air leakage. The cold purge system was equipped with a flowmeter connected to a vent, plus a magnehelic gauge, to monitor excess nitrogen flow out of the desiccator box. The oven in the hot purge system was not an air-tight unit. It was therefore not possible to monitor excess nitrogen flow as was done on the cold purge. Inlet nitrogen flow was adjusted to several different flowrates and bag samples were collected at each flowrate setting. The bags were measured for oxygen content to determine the nitrogen flowrate that would minimize air leaks into the system without unreasonable consumption of nitrogen. The same inlet nitrogen flow was set for both cold and hot purge cycles.

The weighing process was also a source of air leaks into the system. In the original cold and hot purge procedures, the charcoal was to be weighed approximately every 10 minutes until the weight remained constant. Such frequent interruptions during purging would introduce up to 28 liters of air into the system each time the charcoal container was removed. In addition, the integrity of samples collected under such conditions may be questioned. This would be especially true for hot purge samples in which the heated charcoal would continue to off-gas during the weighing process and possibly reabsorb water.

Repetitive charcoal weight measurements also made it impossible to maintain a stable oven temperature during the hot purge cycle. An alternative method for determining charcoal weight loss was desirable due to the drawbacks associated with repetitively weighing the canister. A Beckman 400 hydrocarbon analyzer was used to continuously monitor total hydrocarbons during charcoal purging. The weight of hydrocarbons being purged from the canister was calculated from hydrocarbon concentration. A weight measurement was still taken before and after charcoal purging to obtain total weight loss.

B. Practice Cold and Hot Purge Cycles and Working Capacity Measurement of an In-Use Charcoal Sample

A charcoal sample from a Delco canister which was removed from a 1981 Monte Carlo was subjected to cold and hot purge cycles and to several working capacity cycles. The canister, which was a replacement of the original canister, had accumulated about 10,000 miles of operation.

A 50 g charcoal sample from the canister was cold-purged for a total of 150 minutes and hot-purged for 96 minutes (at ~ 355°F or ~ 180°C) at 42 ℓ/minute. The charcoal container was removed from the sampling system and weighed every 10 minutes during the cold purge. During the hot purge, the charcoal container was weighed after the continuous HC level dropped below 1000 ppmC, at 500 ppmC, and at 300 ppmC. The number of times weight was measured was reduced during the hot purge to minimize oven temperature fluctuations and vapor loss. Hydrocarbon concentrations were monitored continuously during the cold and hot purges. HC concentration, time elapsed, charcoal weight loss, and rate of weight loss are reported in Table 2 for cold and hot purges. The weight loss fell below 1 g/hr at 460 ppmC during the cold purge and at 500 ppmC during the hot purge.

TABLE 2. CONTINUOUS HC CONCENTRATIONS AND RATE OF CHARCOAL WEIGHT LOSS OF IN-USE DELCO CHARCOAL DURING COLD AND HOT PURGE CYCLES

Type of Cycle	Elapsed Time, min	Continuous HC, ppmC	Charcoal Weight Loss, g	Rate of Weight Loss, g/hr
Cold Purge	10	1,100	1.54	9.2
	20	670	0.68	4.1
	30	460	0.15	0.9
	40	430	0.14	0.8
	50	350	0.11	0.7
Hot Purge	10	10,000	--[a]	--[a]
	20	9,300	--[a]	--[a]
	30	4,500	--[a]	--[a]
	40	2,200	--[a]	--[a]
	50	1,300	--[a]	--[a]
	60	840	10.37	10.4
	70	570	--[a]	--[a]
	80	500	0.19	0.6
	90	330	--[a]	--[a]
	96	300	0.06	0.2

---

[a] No measurement taken

Total hydrocarbons were measured on separate bags collected during the cold and the hot purge. The results are listed below. The equation used to calculate grams of hydrocarbons is shown in Appendix C .

Cycle	Total Hydrocarbons Recoveries, g
Cold Purge	1.16
Hot Purge	9.08
Total	10.24 g

Eleven percent of the hydrocarbons measured were produced during the cold purge, and 89 percent were produced during the hot purge. Actual charcoal weight loss during the cold purge was 2.62 g, and 10.62 g was lost during the hot purge, a total greater than the recovered hydrocarbons.

Bag hydrocarbon samples were also analyzed on the HC speciation gas chromatograph. The cold cycle was represented by a predominance of lower molecular weight hydrocarbons in the C_3 to C_6 range. Heavier hydrocarbons in the C_6 to C_{11} range were predominately purged from the canister during the hot purge.

Three alcohols were also measured in the cold and hot purge effluent. The results are given below for methanol, ethanol and TBA:

	Alcohol Recoveries from Used Delco Charcoal, mg		
	Methanol	Ethanol	TBA
Cold Purge	1.6	--[a]	--[a]
Hot Purge	3.7	--[a]	2.3
Total	5.3	--[a]	2.3

---

[a] Not found at measurable levels

The charcoal sampling system was capable of handling the reduced amount of charcoal without saturating the system. The sensitivities of the alcohol and hydrocarbon analyses were sufficient to measure the concentrations produced by the charcoal.

Butane working capacity was also measured on the Delco charcoal according to the procedure outlined by the EPA Project Officer. However, the working capacity was measured at the conclusion of the hot purge rather than after the cold purge cycle. The canister was subjected to five butane loading-purging cycles. The butane flowrate was set at approximately 1 ℓ/minute for the first load cycle, but was lowered to approximately 280 mℓ/minute to obtain a longer breakthrough time (between 7 and 12 minutes instead of 3 minutes). A Ford test procedure for measuring butane working capacity(3) lists a butane loading rate of about 0.6 ℓ/minute, and an ARCO procedure(3) calls for a butane flowrate of about 3 ℓ/minute. The flowrate of butane that SwRI used is approximately one-tenth of the ARCO flowrate. This also corresponds to SwRI using approximately one-tenth of the total charcoal weight to perform charcoal testing.

Breakthrough times at 100 ppmC, 1000 ppmC, and 10,000 ppmC are listed in Table 3 for the butane loading portion of the working capacity procedure. The first three cycles were performed on one day and the fourth and fifth cycles were performed on the following day. Breakthrough times varied about 20 to 30 percent at each breakthrough level.

TABLE 3. BREAKTHROUGH TIMES OF CHARCOAL USING BUTANE

Breakthrough Concentration	Breakthrough Time by Cycle, min					Average of Cycles 2-5	S.D.	CV.
	1[a]	2[b]	3[b]	4[b]	5[b]			
100 ppmC	2.4	11.6	7.4	6.4	6.6	8.0	2.4	30%
1000 ppmC	2.8	12.5	7.6	7.1	8.2	8.8	2.5	28%
10000 ppmC	3.0	13.7	9.4	8.8	11.3	10.8	2.2	20%

---

[a] Butane flowrate 1ℓ/min

[b] Butane flowrate 280 mℓ/min

This canister was cold-purged after breakthrough at 10,000 ppmC (test canisters were loaded to a 1000 ppmC breakthrough level) until the rate of weight loss was 1 g/hr or less. The butane working capacity procedure specifies that the canister should be purged until the rate of weight loss stabilizes to within 1 g/hr. The cold purge cycle was interrupted at varying intervals and the canister was weighed. The rate of weight loss and continuous hydrocarbon concentrations are reported in Appendix D for each of the cycles.

Butane working capacities for four of the five working capacity tests are given in Table 4. The canister was inadvertently not weighed after loading with butane during the first cycle. Breakthrough times and the weights of butane added (measured by the difference in canister weight before and after loading with butane) are also reported. Butane working capacity is calculated by subtracting the canister weight (after purging) from the loaded weight. As defined by the working capacity procedure provided by the EPA Project Officer, a stable working capacity is achieved when two consecutive working capacities agree within 10 percent of the higher of the two values. As shown in Table 4, working capacity varied considerably. Between cycles 3 and 4, the working capacity repeated within 5 percent. However, since the tests were performed on two separate days, working capacity was measured a fifth time to confirm repeatability. Working capacity increased 20 percent from the fourth test. The data obtained from this canister indicate that a working capacity stable to within 10 percent may not be achieved within a reasonable number of cycles as seen in Table 4. Therefore, total of three working capacity cycles was performed on each test canister. The average of the three cycles was calculated.

TABLE 4. BUTANE WORKING CAPACITY OF IN-USE DELCO CHARCOAL

Working Capacity Cycle	Breakthrough Time, min.	Butane Added to Breakthrough, g	Working Capacity, g	Percent Difference From Higher W.C.
1	2.8	--	--	
2	12.5	6.95	6.94	--
3	7.6	5.26	5.25	-24%
4	7.1	4.98	4.98	-5%
5	8.2	6.25	6.20	+20%

C. Validation of the Charcoal Sampling System

Several recovery experiments were conducted on new Delco and Motorcraft canister charcoal. Known quantities of gasoline, alcohols, and water were individually added to dried charcoal samples. The charcoal was then purged at room temperature and under heated conditions at about 340°F (170°C), and the effluent was collected and analyzed. The recoveries are shown in Table 5. The gasoline recoveries were somewhat lower than expected, so additional tests were conducted with no charcoal present. Three gasoline samples (a 5 mℓ sample and two 2.5 mℓ samples) were subjected to separate hot purge cycles (oven temperature ~345°F or ~175°C). The gasoline was pipetted into a 25 mℓ volumetric flask, the flask was placed in the oven and purged until it gave a continuous hydrocarbon reading of less than 500 ppmC. After purging, a gasoline residue remained in the flask; 9 percent of the original

TABLE 5. RECOVERIES OF GASOLINE, METHANOL, ETHANOL, TBA, AND WATER FROM NEW DELCO AND MOTORCRAFT CHARCOALS

Added	Percent Recovered	
	Delco	Motorcraft
4 mℓ unleaded gasoline	73%	66%
0.5 mℓ methanol[a]	84	87
2 mℓ methanol	87	103
2 mℓ methanol	92	--[b]
1 mℓ ethanol	92	96
1 mℓ ethanol	95	--[b]
1 mℓ TBA	89	71
1 mℓ TBA	96	--[b]
4 mℓ water	106	104

---

[a] The methanol recovery from Delco charcoal using 0.5 mℓ methanol was measured during a hot purge only

[b] No measurement

5 mℓ sample and 14 and 16 percent from the 2.5 mℓ gasoline samples. The fraction of volatilized gasoline recovered is listed below. The calculation for determining recovery is shown in Appendix C.

Original Amount of Gasoline, mℓ	Gasoline Evaporated, mℓ	Gasoline Recovered, mℓ	Percent Recovered (no charcoal used)
5.0	4.5	3.5	77%
2.5	2.1	1.7	81%
2.5	2.1	1.5	74%
		Average	77%

The recovery without charcoal was higher than recoveries from Delco (73 percent) or Motorcraft (66 percent) charcoals, however, it was not significantly improved.

Another recovery test was performed using 4 mℓ of pentane without charcoal. The pentane was pipetted into a 25 mℓ volumetric flask and hot-purged until all of the pentane evaporated. The recovery of pentane was 89 percent, about 12 percent higher than the recovery of gasoline. The lower gasoline recovery from the sampling system might be due to the loss of some of the heavier compounds in gasoline to the walls of the sampling system. The lower gasoline recoveries from charcoal may be partially due to the gasoline residue which has a boiling point above the temperature used, and which cannot be accounted for.

A third recovery test was performed using 4 mℓ of 4-methyloctane (C_9) in the hot purge system with no charcoal. The test was conducted in a manner similar to previous recovery tests. The recovery, excluding unevaporated residue, was 86 percent, only slightly lower than that for pentane. The sampling system apparently does not retain significantly greater quantities of the higher molecular weight C_9 compound than pentane, a C_5 compound.

Validation tests were typically of shorter duration than sample charcoal tests because the validation tests were characterized by a more rapid hydrocarbon purge rate than charcoal sample tests. As stated earlier, however, even through purge length varied, the length of the test was a function of final hydrocarbon concentration in the effluent. The difference in test length resulted in validation tests being conducted at a slightly lower temperature than sample tests (170-175°C versus 180-190°C). This was due to the fact that the oven temperature gradually increased over time. The purge temperature was maintained below 200°C because Teflon tubing softens at approximately 200°C.

D. Water Content of New Unused Charcoal

Charcoal from unused evaporative canisters was purged to determine the water content. The charcoal from two Delco canisters, two Motorcraft canisters and one Mopar canister was tested. The fraction of water as a percentage of initial charcoal weight is shown in Table 6.

TABLE 6. WATER CONTENT OF UNUSED CHARCOAL

Charcoal Sample	Percent Water[a]
Delco 1	8%
Delco 2	8%
Motorcraft 1	5%
Motorcraft 2	6%
Mopar	12.5%

---

[a] Weight of water as a percent of initial charcoal weight

The first Delco (GM) charcoal sample was hot-purged (at about 340°F or 170°C) at 23 ℓ/min for 22 minutes. The charcoal lost about 29 g of weight and produced large amounts of water. The weight loss was 8 percent of the original charcoal weight.

The second Delco charcoal sample was both cold- and hot-purged. The cold purge was carried out at room temperature, with a nitrogen flowrate of 23 ℓ/min for 30 minutes. The charcoal was then subjected to a heated purge 340°F (170°C) at 23 ℓ/min for about 30 minutes. The weight loss during the cold purge was about 4 g, and weight loss during the hot purge was 31 g, for a total of 35 g. This mass was 8 percent of the original charcoal weight.

Cold and hot purges were conducted on charcoal from two unused Motorcraft (Ford) canisters and on charcoal from an unused Mopar (Chrysler) canister. One of the Motorcraft charcoal samples was cold purged (at room temperature) for 30 minutes, and then hot-purged on two subsequent 30 minute cycles (~300°F or 150°C) to determine water weight loss. Nitrogen flowing at about 18 /min was used to purge the canister. The charcoal weight loss during each cycle is listed below.

Cold Purge	3.1 g
Hot Purge 1	15.3 g
Hot Purge 2	0.7 g
Total	19.1 g

The total weight loss represented 5 percent of total charcoal weight (377.5 g).

Charcoal from the second Motorcraft canister was hot purged for 60 minutes (~330°F or ~165°C) and it lost 23.4 g of its original 401.7 g mass, or about 6 percent water weight. The Mopar (Chrysler) charcoal was hot purged for 40 minutes, and weight loss was 40.3 g of its original 321.4 g mass, or about 12.5 percent water content.

Mopar charcoal had the highest water content of the three charcoal types. Delco and Motorcraft charcoals had lower, relatively similar water content values. The water content of unused charcoal was typically higher than that of the in-use charcoal samples tested by a few percent. Apparently water is displaced to some degree with fuel vapors when the canister is used on the evaporative system of vehicles.

E. Surface Area of Unused Charcoal Samples

For added information, two new, unused charcoal samples were also analyzed for surface area. A Micromeritics Flowsorb II 2300 was used in the analyses. The surface area of two samples each of Delco and Motorcraft charcoals were measured. Surface areas are shown below on a per gram basis and for the charcoal contained in a standard size canister.

Charcoal Type	Average Surface Area, m^2/g	Total Surface Area of a Standard Size Canister, m^2 [a]
Delco	1388	0.61×10^6
Motorcraft	1074	0.44×10^6

---

[a] Charcoal weight of a typical standard canister was measured in a previous EPA Project,(4) Delco ≈438 g, Motorcraft ≈407 g

The Delco charcoal surface area per gram of charcoal was 29 percent greater than the surface area of Motorcraft charcoal. The total surface area of Delco charcoal in a typical size canister is 39 percent greater than the surface area of Motorcraft charcoal in a typical size canister.

IV. RESULTS

The emissions measured during cold and hot purging of samples of in-use evaporative canister charcoal are listed and discussed in this section. Water content, methanol, ethanol, TBA, total hydrocarbons, and selected detailed hydrocarbons were measured in the effluent sampled from evaporative charcoal. Charcoal working capacity was also measured using butane. The analytical and working capacity data are summarized in Table 7. Individual working capacities are reported in Appendix E. The water, alcohol, total HC, and working capacity data are compared by canister fleet and fuel type in Table 8, by canister vehicle class and fuel type in Table 9, and by cold purge and hot purge in Table 10. In addition, total charcoal weight loss is compared to the sum of water, methanol, ethanol, TBA, and hydrocarbon emissions in Table 11. The distribution of selected detailed hydrocarbons is also compared by canister fleet and fuel type and by cold purge and hot purge (Tables 12 and 13).

Fifty-gram charcoal samples from ten TVA canisters, eight DOE canisters, and six EPA canisters were each subjected to a cold purge cycle, three butane working capacity cycles, and a hot purge cycle. Effluent emissions were measured during the cold purge and the third working capacity cycle of six of the TVA canisters (2090, 2099, 1991, 2067, and 8961). All 24 canister samples had emissions measured during the hot purge cycle.

Emissions in Tables 8, 9, and 10 were averaged, and standard deviations and coefficients of variation were calculated for the different groupings of data. Test results from EPA canisters with unknown fuel histories (A1480008, 0049, 0073, 0039, and 0060) were grouped under the gasoline heading. Significant overlap between average values occurred at the 95 percent confidence level. The 95 percent confidence interval is approximately ± 2 standard deviations about the average. Relative comparisons can be made, however.

A. Water Content

Charcoal water content did not differ significantly between canisters exposed to gasoline vapors and canisters exposed to an alcohol blend. As seen in Table 8, 50 g of TVA charcoal produced an average of 1 g of water and 50 g samples of DOE charcoal an average of 0.5 to 0.6 g of water from each type of canister. EPA canisters of unknown fuel history produced an average of 0.5 g of water. An insufficient number of EPA blend charcoal samples were analyzed to make a comparison.

Average water content of Chevy Chevette (TVA) blend charcoal samples (1.3 g) was slightly higher than that from gasoline charcoal samples (1.1 g) as shown in Table 9. Ford Escort (DOE fleet) gasoline and blend charcoals produced nearly equivalent levels of water (0.6 and 0.5 g). An insufficient number of gasoline and blend charcoal samples from the Ford Fairmonts (TVA fleet) and 83 Fords (EPA fleet) were analyzed to make comparisons. Between vehicle classes, gasoline Chevy Chevette (TVA fleet) charcoal had the highest water content (1.1 g), followed by Ford Escort (DOE fleet) charcoal (0.6 g), and 83 Ford with DFM3.31GXFX (EPA fleet) charcoal (0.3 g). Among blend vehicle

TABLE 7. SUMMARY OF RESULTS OF IN-USE EVAPORATIVE CANISTER CHARCOAL TESTING ON 50 g SAMPLES OF CHARCOAL

Vehicle Fuel Type	Canister Number	Cold Purge Cycle					Working Capacity Cycle		Hot Purge Cycle				
		Water, g	Alcohols, mg			Total HC, g	Total HC, g	Average Working Capacity, g	Water, g	Alcohols, mg			Total HC, g
			Methanol	Ethanol	TBA					Methanol	Ethanol	TBA	
Gasoline	TVA												
	2090	0.70	3	<1	11	1.11	1.31	2.41	1.59	19	8	43	14.22
	2099	1.19	2	<1	25	1.49	1.19	2.39	1.48	20	<1	95	11.50
	1925						a	2.19	0.20	5	<1	12	9.18
	8887	0.57	1	<1	8	1.21	1.51	1.55	0.74	9	<1	2	3.74
Blend	1991	1.08	3	<1	68	1.48	2.00	2.18	1.48	65	<1	71	11.69
	2067	0.74	4	<1	27	1.43	1.02	2.48	1.16	34	<1	43	16.48
	1725						a	2.41	1.72	4	<1	< 1	8.21
	1747						a	1.66	0.88	34	<1	9	18.90
	8961	0.40	4	<1	12	3.27	1.00	1.37	0.59	20	<1	1	7.68
	8902						a	1.55	0.48	17	<1	1	6.94
Gasoline	DOE												
	201						a	2.07	0.30	1	1	1	6.98
	202						a	1.91	0.39	3	<1	7	6.95
	205						a	2.01	1.17	10	2	1	7.81
	206						a	1.34	0.38	12	2	5	6.13
Blend	101						a	1.43	0.49	23	4	2	6.58
	102						a	1.77	0.20	42	8	3	6.81
	104						a	2.11	0.67	31	9	5	6.13
	106						a	1.90	0.58	31	8	2	_b
Unknown	EPA												
	A1480008						a	1.24	_b	15	<1	< 1	5.55
	A1480049						a	1.54	0.29	1	20	< 1	5.58
	A1480073						a	1.75	0.40	1	38	< 1	6.56
	A1480039						a	1.82	0.30	2	1	2	5.82
	A1480060						a	2.22	0.81	38	16	46	6.26
Blend	A1480096						a	1.73	0.70	32	2	27	6.84

---

[a] Not measured

[b] No Data

TABLE 8. COMPARISON OF CHARCOAL HOT PURGE CYCLE EMISSIONS AND WORKING CAPACITY BY FLEET AND VEHICLE FUEL TYPE FOR 50 g SAMPLES OF CHARCOAL

		Gasoline						Blend					
			Alcohols, mg						Alcohols, mg				
Fleet		Water, g	Methanol	Ethanol	TBA	Total HC, g	Average Working Capacity, g	Water, g	Methanol	Ethanol	TBA	Total HC, g	Average Working Capacity, g
TVA	Avg.	1.00	13	2	38	9.66	2.14	1.05	29	1	21	11.6	1.94
	S.D.[a]	0.65	7	4	42	4.45	0.40	0.49	21	0	30	5.0	0.47
	C.V.[b]	65%	56%	200%	110%	46%	19%	47%	72%	0%	141%	43%	24%
DOE	Avg.	0.56	6	1	4	6.97	1.83	0.49	32	7	3	6.51	1.80
	S.D.[a]	0.41	5	1	3	0.69	0.33	0.20	8	2	1	0.35	0.29
	C.V.[b]	73%	89%	80%	75%	10%	18%	42%	24%	31%	47%	5%	16%
EPA	Avg.	0.45	11	15	10	5.95	1.71	0.70	32	2	27	6.84	1.73
	S.D.[a]	0.25	16	16	20	0.44	0.3	—	—	—	—	—	—c
	C.V.[b]	54%	146%	104%	200%	7%	21%	—	—	—	—	—	—c

---

[a] S.D. = standard deviation

[b] C.V. = coefficient of variation as a percent

[c] Insufficient number of samples to calculate standard deviation and coefficient of variation

TABLE 9. COMPARISON OF CHARCOAL HOT PURGE EMISSIONS AND WORKING CAPACITY BY VEHICLE CLASS AND FUEL TYPE FOR 50 g SAMPLES OF CHARCOAL

		Gasoline							Blend					
			Alcohols, mg							Alcohols, mg				
Vehicle Description	Canister Number	Water,g	Methanol	Ethanol	TBA	Total HC, g	Average Working Capacity,g	Canister Number	Water,g	Methanol	Ethanol	TBA	Total HC, g	Average Working Capacity,g
81, 82 Chevy Chevette 98 CID	TVA 2090	1.59	19	8	43	14.22	2.41	TVA 1991	1.48	65	<1	71	11.69	2.18
	TVA 2099	1.48	20	<1	95	11.50	2.39	TVA 2067	1.16	34	<1	43	16.48	2.48
	TVA 1925	0.20	5	<1	12	9.18	2.19	TVA 1725	1.72	4	<1	<1	8.21	2.41
								TVA 1747	0.88	34	<1	9	18.90	1.66
	Avg.	1.09	15	3	50	11.6	2.33		1.31	34	<1	31	13.8	2.18
	S.D.[a]	0.77	8	5	42	2.5	0.12		0.37	25	0	33	4.8	0.37
	C.V.[b]	71%	56%	154%	84%	22%	5%		28%	73%	0	105%	35%	17%
81 Ford Fairmont Wagon 140 CID	TVA 8887	0.74	9	<1	2	3.74	1.55	TVA 8961	0.59	20	<1	1	7.68	1.37
								TVA 8902	0.48	17	<1	1	6.94	1.55
	Avg.	0.74	9	<1	2	3.74	1.55		0.54	18	<1	1	7.31	1.46
	S.D.[a]	c	c	c	c	c	c		c	c	c	c	c	c
	C.V.[b]	c	c	c	c	c	c		c	c	c	c	c	c
84 Ford Escort 98 CID	DOE 201	0.30	1	1	1	6.98	2.07	DOE 101	0.49	23	4	2	6.58	1.43
	DOE 202	0.39	3	<1	7	6.95	1.91	DOE 102	0.20	42	8	3	6.81	1.77
	DOE 205	1.17	10	2	1	7.81	2.01	DOE 104	0.67	31	9	5	6.13	2.11
	DOE 206	0.38	12	2	5	6.13	1.34	DOE 106	0.58	31	8	2	—[d]	1.90
	Avg.	0.56	6	1	4	6.97	1.83		0.49	32	7	3	6.51	1.80
	S.D.[a]	0.41	5	1	3	0.69	0.33		0.20	8	2	1	0.35	0.29
	C.V.[b]	73%	89%	96%	75%	10%	18%		42%	24%	31%	47%	5%	16%
83 Ford DFM3.3V1GXFX	EPA A1480008	—[d]	15	<1	<1	5.55	1.24							
	0049	0.29	1	20	<1	5.58	1.54							
	0073	0.40	1	38	<1	6.56	1.75							
	0039	0.30	2	1	2	5.82	1.82							
	Avg.	0.33	5	15	<1	5.88	1.59							
	S.D.[a]	0.06	7	18	1	0.47	0.26							
	C.V.[b]	18%	137%	120%	200%	8%	16%							
83 Ford DFM3.3V1GEF6	EPA A1480060	0.81	38	16	46	6.26	2.22	EPA A1480096	0.70	32	2	27	6.84	1.73

---

[a] S.D. = standard deviation
[b] C.V. = coefficient of variation as a percent
[c] Insufficient data to calculate standard deviation or coefficient of variation
[d] No Data

TABLE 10. COMPARISON OF COLD PURGE CYCLE AND HOT PURGE CYCLE TVA CHARCOAL SAMPLE EMISSIONS FOR 50 g SAMPLES OF CHARCOAL[a]

		Cold Purge Cycle					Hot Purge Cycle				
			Alcohols, mg					Alcohols, mg			
Canister	Vehicle Fuel Type	Water,g	Methanol	Ethanol	TBA	Total HC, g	Water,g	Methanol	Ethanol	TBA	Total HC, g
TVA 2090	Gasoline	0.70	3	1	11	1.11	1.59	19	8	43	14.22
TVA 2099	Gasoline	1.19	2	1	25	1.49	1.48	20	1	95	11.50
TVA 8887	Gasoline	0.57	1	1	8	1.21	0.74	9	1	2	3.74
Avg.		0.82	2	1	15	1.27	1.27	16	3	47	9.82
S.D.[b]		0.33	1	0	9	0.20	0.46	6	5	47	5.44
C.V.[c]		40%	50%	0	60%	16%	36%	38%	2	100%	55%
TVA 1991	Blend	1.08	3	1	68	1.48	1.48	65	1	71	11.69
TVA 2067	Blend	0.74	4	1	27	1.43	1.16	34	1	43	16.48
TVA 8961	Blend	0.40	4	1	12	3.27	0.59	20	1	1	7.68
Avg.		0.74	4	1	36	2.06	1.06	40	1	38	11.95
S.D.[b]		0.34	1	0	29	1.05	0.45	23	0	35	4.41
C.V.[c]		46%	14%	0	81%	51%	42%	58%	0	93%	37%

---

[a] This table includes only charcoal samples that received both cold purge and hot purge analyses. Table 7 shows individual sample data for these as well as the samples that received only hot purge analyses.

[b] S.D. = standard deviation

[c] C.V. = coefficient of variation as a percent

TABLE 11. COMPARISON OF CHARCOAL WEIGHT LOSS AND TOTAL RECOVERED WEIGHT DURING COLD AND HOT PURGE CYCLES FOR 50 g SAMPLES OF CHARCOAL[a]

		Cold Purge			Hot Purge		
Vehicle Fuel Type	Canister Number	Charcoal Weight Loss, g	Total Recovered Weight, g	Percent Difference[b]	Charcoal Weight Loss, g	Total Recovered Weight, g	Percent Difference[b]
Gasoline	TVA 2090	1.87	1.82	-3	10.16	15.88	+56
	TVA 2099	2.16	2.71	+25	9.82	13.10	+33
	TVA 1925	2.13	--[c]		8.78	9.40	+7
	TVA 8887	1.39	1.79	+29	7.97	4.49	-44
Blend	TVA 1991	2.15	2.63	+22	10.78	13.31	+24
	TVA 2067	2.29	2.20	-4	10.72	17.72	+65
	TVA 1725	2.93	--[c]		8.88	9.93	+12
	TVA 1747	3.48	--[c]		9.24	19.82	+114
	TVA 8961	3.34	3.69	+11	7.63	8.29	+9
	TVA 8902	0.75	--[c]		7.49	7.43	-1
Gasoline	DOE 201	5.3[d]	--[c]		7.14	7.28	+2
	DOE 202	6.63	--[c]		6.81	7.35	+8
	DOE 205	5.33	--[c]		7.81	8.99	+15
	DOE 206	6.34	--[c]		6.31	6.53	+4
Blend	DOE 101	6.42	--[c]		6.72	7.10	+6
	DOE 102	6.31	--[c]		6.85	7.06	+3
	DOE 104	7.93	--[c]		6.67	6.85	+3
	DOE 106	5.19	--[c]		7.19	--[e]	
Unknown	EPA 1480008	4.91	--[c]		5.69	--[f]	
	EPA 1480049	4.88	--[c]		6.12	5.89	-4
	EPA 1480073	4.19	--[c]		6.53	7.00	+7
	EPA 1480039	3.52	--[c]		6.37	6.13	-4
	EPA 1480060	3.89	--[c]		6.52	7.17	+10
Blend	EPA 1480096	6.04	--[c]		6.83	7.60	+11

---

[a] Recovered weight = sum of the weights of water, methanol, ethanol, TBA, and total HC purged from charcoal samples

[b] Percent difference calculated relative to charcoal weight loss

[c] Not measured

[d] Measured to one decimal place only

[e] Total hydrocarbons not measured

[f] Water content not measured

classes with a sufficient number of individual charcoal samples to make comparisons, Chevy Chevette charcoal had a higher water content than Ford Escort charcoal, 1.3 g and 0.5 g, respectively. There was no apparent difference in hot purge to cold purge water ratio between Chevette (GM) charcoal and Fairmont (Ford) charcoal.

Hot purge cycle water emissions were somewhat higher than cold purge water emissions for the TVA canisters shown in Table 10 for both gasoline and blend samples. Water content from gasoline hot purge averaged 1.3 g, while cold purge water content averaged 0.8 g. Blend hot purge water content was 1.1 g versus 0.7 g from the cold purge.

B. Methanol, Ethanol, and TBA

Varying amounts and proportions of the three alcohols were found in charcoal effluent samples. As shown in Table 7, methanol was measured in all samples in quantities ranging from 1 to 65 mg. Less than 1 mg of ethanol was present in 17 of 30 analyses. In the remaining samples, ethanol was measured at levels from 1 to 38 mg. Measurable quantities of TBA were found in all but 4 samples, with amounts ranging from 1 to 95 mg. Considerable variation from the mean value occurred for most groups of samples. In addition, the ranges of values at the 95 percent confidence level overlapped for most sample groups.

Quantities of methanol, ethanol, and TBA were averaged by fleet and fuel type. Standard deviations and coefficients of variation were also calculated. These values are reported in Table 8. A method for determining the extent of alcohol "contamination" of evaporative charcoal consists of a comparison of the alcohol content in the charcoal effluent relative to the alcohol content in the fuel. Enrichment of alcohol in the charcoal effluent indicates charcoal retention and "contamination." The blend TVA canisters had been tested using a 5 percent O_2 gasoline-alcohol blend. The oxygen content of effluent on the TVA blend charcoal samples due to methanol, ethanol, and TBA was approximately 0.4 percent (of total hydrocarbons). The alcohol content of the blend fuel used on the DOE blend vehicles was 9 percent by weight. The fraction of alcohol measured on the DOE blend charcoal effluents was only 0.6 percent of total measured hydrocarbons. Enrichment of alcohols on the blend TVA and DOE charcoals apparently did not occur. Since the fuel history of the EPA canisters was not known, similar enrichment comparisons could not be made.

Methanol, ethanol, and TBA were also found in measurable quantities on gasoline-exposed charcoal samples. This situation was particularly noticeable with the TVA charcoals, in which roughly equivalent levels of total alcohols were found on both gasoline and blend charcoals (53 mg and 50 mg, respectively). TBA made up 72 percent of total alcohols present in TVA gasoline charcoals, whereas TBA from DOE gasoline charcoals was 36 percent of total alcohols. The presence of alcohols on the gasoline charcoals can be an indication of vehicle cross-fueling, or possibly the accumulation of low levels of alcohol from gasoline over an extended period of time. All DOE canisters had been subjected to a SHED test using a gasoline-blend fuel. The total alcohol content of DOE blend charcoals was approximately four times that of DOE gasoline charcoals (42 mg versus 11 mg). Average methanol was about five times higher (32 mg versus 6 mg) and average ethanol was about seven times higher (7 mg versus 1 mg) than from DOE gasoline charcoals. TBA emissions did not vary appreciably between blend and gasoline charcoals, 3 mg and 4 mg, respectively.

The EPA canister charcoals produced alcohols in proportions that may be an indicator of fueling histories. As shown in Table 7, A1480008 charcoal effluent emitted 15 mg of methanol and unmeasurable amounts of ethanol and TBA. Samples A1480049 and A1480073 produced 20 mg and 38 mg of ethanol but negligible levels of methanol and TBA. Sample A1480039 emitted 2 mg or less of the three alcohols, while sample A1480060 produced measurable amounts of each alcohol. A1480096 charcoal, which was from a vehicle known to have been fueled at least briefly with a gasoline/methanol/TBA blend, produced larger amounts of methanol and TBA, 32 mg and 27 mg respectively, than ethanol (2 mg).

As seen in Table 9, charcoal samples from the gasoline Chevy Chevettes (TVA fleet) emitted, on average, higher levels of methanol (15 mg vs. 6 mg) and TBA (50 mg vs. 4 mg) than charcoal samples from the gasoline Ford Ecorts (DOE fleet). Average ethanol purge emissions were similar for the Chevettes (3 mg) and the Escorts (1 mg). With the blend samples, the Chevette and Escort charcoals produced nearly equal amounts of methanol (34 mg and 32 mg) when purged. Charcoals from blend Chevette canisters emitted unmeasurable levels of ethanol and an average of 31 mg of TBA when purged. The Escort charcoals produced an average of 7 mg of ethanol and 3 mg of TBA. Overall, the Chevette gasoline and blend charcoals produced total alcohols in excess of Escort gasoline and blend charcoals during purging. A comparison of average alcohol values for charcoal samples from the 1983 Fords with DFM3.3V1GXFX engines and DFM3.3V1GEF6 engines would not be informative because of the widely varying alcohol levels produced.

Alcohols were measured during the cold purge cycle of six of the TVA charcoals, and from the hot purge cycle of all TVA charcoals. The cold purge and hot purge alcohol emissions are compared in Table 10. Total alcohols produced during the hot purge cycle of gasoline charcoals were almost four times higher than the alcohols emitted during cold purging (66 mg versus 17 mg). The higher hot purge alcohol level relative to the cold purge level was due mainly to higher methanol (16 mg versus 2 mg) and TBA (47 mg versus 15 mg) emissions. Hot purge alcohol emissions from blend samples also exceeded cold purge alcohol emissions by a factor of two (78 mg versus 40 mg). This difference was primarily due to higher methanol emissions (40 mg compared to 4 mg produced during the cold purge cycle).

Comparing gasoline and blend total alcohol emissions during purges, blend charcoals emitted higher levels of alcohols during both the cold and hot purge cycles than the gasoline charcoal samples. Total alcohols from blend charcoals were almost 20 percent higher than from gasoline charcoals. Methanol levels averaged 40 mg versus 16 mg from the gasoline samples, but the amount of TBA averaged 38 mg versus 47 mg from the gasoline samples. The difference was greater in the cold purge, when blend alcohol emissions were approximately double those for charcoal used with gasoline (40 mg compared to 17 mg). Methanol and TBA concentrations contributed to the difference in total alcohols, while ethanol levels did not change. The difference in alcohol emissions from blend relative to gasoline charcoals during the hot purge cycle was less than that in the cold purge cycle.

C. Total Hydrocarbons

Average total hydrocarbon emissions were slightly higher from 50 g samples of TVA blend charcoal than from 50 g samples of TVA gasoline charcoal (11.9 g versus 9.7 g) as shown in Table 8. This difference was not significant at a 90% confidence level. DOE total hydrocarbon emissions were nearly equivalent from gasoline and blend canisters, with an average of 7.0 g from gasoline charcoal and 6.5 g from blend charcoal. On a fleet-to-fleet basis, total hydrocarbons from gasoline canisters were highest from TVA charcoal (9.7 g) and lowest from EPA charcoal (6.0 g). TVA blend charcoals emitted higher levels of total hydrocarbons than DOE blend charcoal samples, 11.9 g versus 6.5 g, respectively. An insufficient number of EPA blend charcoal samples were analyzed to make comparisons.

A comparison can be made between gasoline and blend charcoals by vehicle class. Total hydrocarbon emissions from Chevy Chevette (TVA fleet) blend canisters were, on average, higher than from gasoline canisters, 13.8 g compared to 11.6 g, but this difference was not significant at a 90% confidence level (see Table 9). Total hydrocarbon emissions from Ford Escort (DOE fleet) gasoline and blend charcoal samples were nearly equivalent (7.0 g versus 6.5 g) as mentioned earlier (Ford Escorts make up the entire DOE fleet). The Chevy Chevette gasoline charcoal samples were highest in total hydrocarbon emissions (11.6 g), followed by Ford Escort charcoal (7.0 g), 83 Ford EPA samples (about 6g), and the Ford Fairmont sample (3.74 g). Among the blend canisters, Chevy Chevettes had highest total hydrocarbon emissions (13.8 g) followed by the Ford Fairmont (7.1 g), the Ford EPA sample (6.8 g), and the Ford Escorts (6.5 g).

Hot purge cycle total hydrocarbon emissions exceeded cold purge cycle total hydrocarbon levels for both gasoline and blend TVA canisters. Table 10 shows average total hydrocarbon values of 9.8 g and 1.3 g from the gasoline hot and cold purge cycles, and 12.0 g and 2.1 g from the blend hot and cold purge cycles, respectively. The difference between 9.8 g and 1.3 g from the gasoline hot and cold purge cycles is significant at the 95 percent confidence level.

D. Comparison of Charcoal Weight Loss to the Sum of Water Content, Alcohols, and Total Hydrocarbons

The weights of charcoal samples were measured before and after each purge cycle to determine the mass of materials removed during purging. The recovered weights of water, methanol, ethanol, TBA, and total hydrocarbons were summed, and these values plus charcoal weight losses are reported in Table 11. The percent differences between charcoal weight losses and total recovered weights are also listed. Recovered weights were similar to or exceeded actual weight loss (differences from -4 to +114%) except for the hot purge of charcoal TVA 8887, in which recovered weight was 44 percent lower than charcoal weight loss. The best agreement between recovered weight and charcoal weight loss occurred with DOE and EPA charcoals; the percent differences were all 15 percent or less. Among the DOE charcoals, only one sample (DOE 205) did not agree within 8 percent (recovered mass was 15% higher for DOE 205). This charcoal sample, which was tested after TVA charcoal 1747, may have been subject to hydrocarbon carry-over. TVA 1747 produced the highest level of hydrocarbons of all charcoal samples (see Table 7).

Recovered weight was determined during six cold purge cycles and all hot purge cycles of TVA charcoals. The agreement between charcoal and measured recovered weight of TVA charcoals was not as good as with DOE and EPA charcoals; only 44 percent (7 of 16) of the recovered weights agreed within 15 percent of the charcoal weight losses. For five of the hot purge charcoals, recovered weight exceeded charcoal weight loss by more than 15 percent. Actual weight losses and recovered weights for these charcoals were on the high end of the range of weight losses, with charcoal weight losses exceeding 9 g and recovered weight exceeding 13 g. Three of the cold purge charcoal samples also had recovered weights which were more than 15 percent higher than charcoal weight losses.

The relatively large difference between charcoal weight losses and recovered weights of some of the TVA charcoal samples may be due in part to the higher fraction of unsaturated hydrocarbons in TVA effluent relative to DOE and EPA charcoal effluents. A greater fraction of unsaturated compounds affects the carbon-hydrogen ratio of the effluent, the calculated quantity of hydrocarbons, and therefore, the recovered weight (which is composed of hydrocarbons, water, and alcohols). A comparison of detailed hydrocarbon emissions shows that, on average, a greater fraction of hydrocarbons from hot purged TVA charcoals was unsaturated (60 percent) compared to the hydrocarbons measured in hot purged DOE and EPA charcoal effluent (34-36 percent). Cold purged TVA hydrocarbons were composed of approximately 46 percent unsaturated compounds (this is discussed in more detail in Section F). The higher fraction of unsaturated compounds in TVA charcoal effluent is also consistent with the more intense odor produced by TVA charcoal samples compared to DOE and EPA charcoal samples.

The fraction of unsaturated compounds in the purged effluent affects the density of the hydrocarbon mixture, and thus, the calculated quantity of hydrocarbons. The densities of the DOE and EPA charocal effluents may have more closely approximated the Federal Register fuel density (16.33 g/ft^3) which was used to calculate the hydrocarbon concentrations (it was not practical for this program to use individual hydrocarbon densities to calculate the concentration of each of the 99 hydrocarbons). If the densities of DOE and EPA charcoal effluents were similar to 16.33 g/ft^3, the calculated hydrocarbon values would be a good approximation of the hydrocarbons in the charcoal effluent. This is a possible explanation for the relatively close agreement between recovered weights and charcoal weight losses of DOE and EPA charcoals compared to TVA charcoals. The TVA charcoal effluent, on the other hand, was typically composed of a higher percentage of unsaturated hydrocarbons (which would have a lower density than effluent from the DOE or EPA charcoals). Thus, the calculated hydrocarbon concentrations for TVA charcoals could be overstated. This could explain the relatively high recovered weight compared to the charcoal weight loss of some TVA charcoals.

Another factor which can influence the measurement of hydrocarbon concentrations is the varying tendency of the hydrocarbons to remain in the gaseous state for analysis. The recovery of compounds with boiling points exceeding that of 4-methyloctane (142°C) was not determined for this program. It is possible that some losses could have occurred if higher boiling compounds were emitted by the charcoal, but not recovered as gases for analysis.

Comparing cold and hot purge charcoal weight loss, the weight of effluent removed during hot purging generally exceeded the amount purged during the cold purge cycle. Charcoal weight loss of TVA charcoals from hot purging was 2 to 10 times greater than the weight loss from cold purging. DOE charcoal weight loss from hot purging was also higher than cold purge weight loss (from 3 to 46 percent) for six of the eight charcoals. Of the two remaining charcoal samples, one had equivalent cold and hot purge charcoal weight losses (DOE 206) and one had a hot purge weight loss which was 16 percent lower than the cold purge weight loss (DOE 104). the EPA charcoal samples had hot purge weight losses which were 13 to 81 percent greater than cold purge weight losses. Higher charcoal weight losses from hot purging compared to cold purging is also consistent with the higher total recovered weights which were measured from hot purge cycles.

E. Working Capacity[a]

Average TVA working capacity was slightly higher from gasoline canisters than from blend canisters, 2.1 g and 1.9 g, respectively, as shown in Table 8. No significant difference between DOE gasoline and blend charcoal working capacities was observed (average of 1.8 g each). The average working capacity from the gasoline TVA fleet (2.1 g) was slightly higher than that from the DOE fleet (1.8 g), which was in turn slightly higher than that from the EPA fleet (1.7 g). The average TVA blend working capacity was 0.1 g higher than the DOE blend (1.9 g versus 1.8 g).

Working capacity of 50 g charcoal samples from gasoline Chevy Chevette canisters was slightly higher than from the blend Chevy Chevette (2.3 g compared to 2.2 g), while the Ford Escorts had equivalent working capacities (1.8 g) for gasoline and blend canisters, as seen in Table 9. Among gasoline canisters, Chevy Chevette charcoal samples had a higher average working capacity (2.3 g) than Ford Escorts (1.8 g), which was higher than that of the 83 Fords with DFM3.3V1GXFX engines (1.6 g). With the blend fuel, Chevy Chevette charcoals also had a higher average working capacity compared to the Ford Escort charcoals, 2.2 g versus 1.8 g.

F. Detailed Selected Hydrocarbons

A detailed hydrocarbon analysis was performed on charcoal effluent from several cold and all hot purges. A sample chromatogram is shown in Figure 4. The calculated weight of each compound for each sample is listed in Appendices

---

[a] Working capacities were measured and are reported as grams of HC per 50 gram charcoal sample. This measure may be slightly misleading since the "50 gram" samples were weighed prior to the first cold purge. Therefore, the 50 grams included the mass of whatever adsorbed compounds were present which varied from approximately five to fifteen grams, depending on the sample.

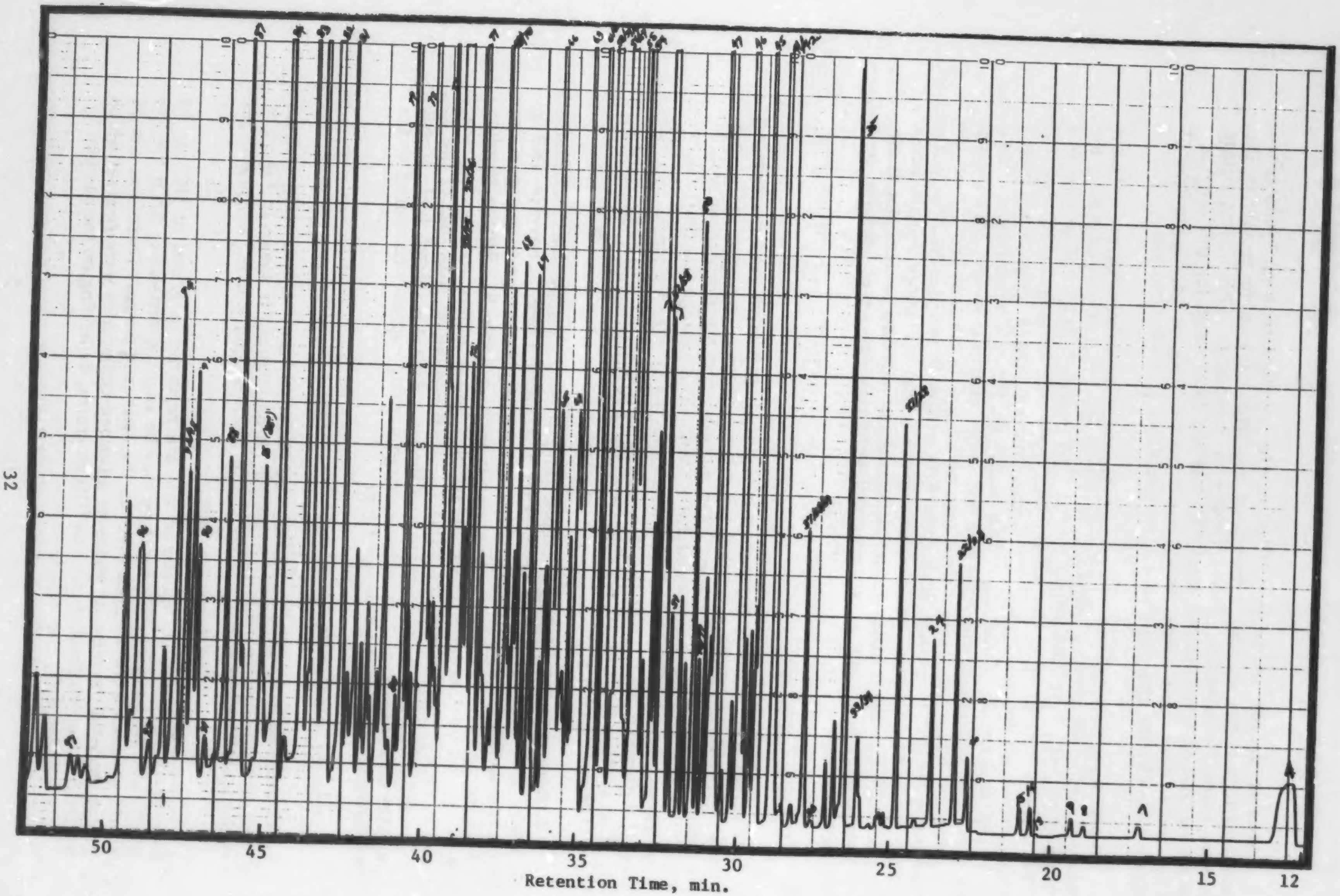


Figure 4. Selected detailed hydrocarbon chromatogram for Canister Number EPA A1480049 hot purge cycle, diluted ~1 to 10

F-1 through F-4. The weights were calculated based on the fraction of the GC peak area of each compound (or each group of inseparable compounds) to total peak area multiplied by the total hydrocarbon weight (found in Table 7). The fractions are listed in Appendices F-5 through F-9. Hydrocarbon speciation was also performed on several working capacity cycles, but the only compound recovered at measurable levels was butane.

The hydrocarbon peaks were grouped to more clearly understand the volume of data. The peaks were classified into five groups based on the general distribution of the data. The groups are described below.

Compound Number	Approximate Carbon Number
40	C_3 to C_6
41-55	C_7 to C_8
56-72	C_8, C_9
73-84	C_9
85-99	C_{10}, C_{11}

Compound numbers refer to the list of compounds in Table 12. The percentages calculated for Appendices F-5 through F-9 were summed for each charcoal sample. The percentages were also summed for each group, and the group total was divided by the canister total to determine the percentage of each hydrocarbon group to total detailed hydrocarbons. The resulting data, which are shown in Table 13, were plotted to provide a visual display of the distribution of hydrocarbon species.

The percentages in each hydrocarbon group were averaged by fleet and fuel type, and standard deviations and coefficients of variation were calculated. Overlap occurred for most data at the 95 percent confidence level, however, an obvious difference in the distribution of hydrocarbons is evident between fleets as shown in Figure 5. The data represented are from hot purge cycle emissions. The TVA charcoal samples produced predominantly heavier hydrocarbons in the C_9 to C_{11} range. The distribution curves from TVA gasoline and blend charcoal were very similar. DOE charcoal produced a more even distribution of each group of hydrocarbons than TVA charcoal. The distribution curve from DOE blend charcoal was weighted slightly more toward the heavier C_9 compounds than the DOE gasoline curve. The averaged hydrocarbon distribution from EPA charcoal samples was very similar between gasoline and blend canisters. Both produced "M" shaped distributions which were weighted more toward C_7 to C_8 compounds and C_9 compounds. The distribution of hydrocarbons purged from the charcoal gives an indication of the loading characteristics for each fleet. The TVA canisters were loaded with more of the heavier hydrocarbons than the DOE or EPA canisters.

A comparison of detailed hydrocarbon emissions was made for cold and hot purged TVA charcoal. Figure 6 shows the distribution of hydrocarbons for six canister samples. Cold purge data from TVA 2090 were not available. The cold purge cycle produced a higher percentage of C_3 to C_8 compounds and the hot purge cycle emitted more of the C_9 to C_{11} compounds. An "M" shaped curve was apparent for three of the cold purge charcoal samples, TVA 2099,

TABLE 12. COMPOUND NUMBERS FOR SELECTED DETAILED HYDROCARBONS

1. Methyl Acetylene
2. Isobutane
3. Isobutene
4. n-Butane
5. trans-2-butene
6. cis-2-butene
7. Isopentane
8. 1-pentene
9. Pentane
10. 2-Methyl-1-butene
11. Isoprene(2-Methyl-1,3-butadiene)
12. trans-2-pentene
13. cis-2-pentene
14. 2-Methyl-2-butene
15. 2,2-Dimethylbutane
16. Cyclopentene
17. Cyclopentane
18. 3-Methyl-1-pentene
19. 4-Methyl-1-pentene
20. 2,3-Dimethylbutane
21. 2,3-Dimethyl-1-butene
22. 2-Methylpentane
23. 4-Methyl-2-pentene
24. 3-Methylpentane
25. 2-Methyl-1-pentene
26. 1-Hexene
27. Hexane
28. 2-Ethyl-1-butene
29. cis-3-Hexene
30. 2-Methyl-2-pentene
31. cis-3-methyl-2-pentene
32. cis-2-hexene
33. 1-Hexyne
34. trans-3-methyl-2-pentene
35. 2,4-Dimethylpentane
36. Methylcyclopentane
37. Benzene
38. Cyclohexane
39. Methylcyclopentene
40. 3-Methyl-1,3-pentadiene
41. 2,3-Dimethylpentane
42. 2-Methylhexane
43. Cyclohexene
44. 5-methyl-2-hexene
45. 3-Methylhexane
46. 2,2,4-Trimethylpentane
47. n-Heptane
48. 2,4,4-Trimethyl-1-pentene
49. 2,2,4-Trimethyl-1-pentene
50. Methylcyclohexane
51. 2,4,4-Trimethyl-2-pentene
52. 2,4-Dimethylhexane
53. 2,5-Dimethylhexane
54. 2,3,4-Trimethylpentane
55. 2,3,3-Trimethylpentane
56. Toluene
57. 2-Methyl-3-heptene
58. 3,5,5-Trimethyl-1-hexene
59. 2-Methylheptane
60. 4-Methylheptane
61. 3-Methylheptane
62. 2,5-Dimethyl-1,5-hexadiene
63. 2,2,5-Trimethylhexane
64. 2-Ethyl-1-hexene
65. 1-cis-4-Dimethylcyclohexane
66. Octane
67. 2,3,5-Trimethylhexane
68. 2,4-Dimethylheptane
69. 2,5-Dimethylheptane
70. 3,5-Dimethylheptane
71. Ethylbenzene
72. 2,3-Dimethylheptane
73. p-Xylene
74. m-Xylene
75 2-Methyloctane
76. 4-Methyloctane
77. 3-Methyloctane
78. o-Xylene
79. Nonane
80. trans-2-nonene
81. Propylbenzene
82. 2,3-Dimethyloctane
83. o-Ethyltoluene
84. 1,2,4-Trimethylbenzene
85. Isobutylbenzene
86. Decane
87. p-Cymene
88. Indan(e)
89. 4-Phenyl-1-butene
90. m-Diethylbenzene
91. 1-Methyl-3-propylbenzene
92. n-Butylbenzene
93. p-Diethylbenzene
94. o-Diethylbenzene
95. 2-Methyldecane
96. Bicyclopentyl
97. Undecane
98. 1,2,3,4-Tetramethylbenzene
99. Pentylbenzene

TABLE 13. PERCENTAGE OF EACH HYDROCARBON GROUP TO TOTAL DETAILED HYDROCARBONS[a]

Cold Purge Cycle

Gasoline Canister Number	<40	41-55	56-72	73-84	85-99
TVA 2090	--[b]	--	--	--	--
TVA 2099	8	31	23	29	10
TVA 8887	34	20	10	26	11
Avg.	21	26	16	28	10
S.D.[c]	e	e	e	e	e
C.V.(%)[d]	e	e	e	e	e

Blend Canister Number	<40	41-55	56-72	73-84	85-99
TVA 1991	<1	16	33	43	9
TVA 2067	3	23	14	39	9
TVA 8961	14	35	19	23	8
Avg.	6	25	22	42	9
S.D.[c]	7	10	10	18	1
C.V.(%)[d]	123	38	45	43	6

Hot Purge Cycle

Gasoline Canister Number	<40	41-55	56-72	73-84	85-99
TVA 2090	<1	<1	3	59	38
TVA 2099	2	2	12	60	25
TVA 8887	<1	15	23	52	9
TVA 1925	<1	<1	4	55	41
Avg.	0.5	4	11	57	28
S.D.[c]	1.0	7	9	4	15
C.V.(%)[d]	200	175	93	7	52

Blend Canister Number	<40	41-55	56-72	73-84	85-99
TVA 1991	<1	<1	2	63	35
TVA 2067	<1	<1	3	63	34
TVA 8961	<1	13	27	53	8
TVA 1725	<1	4	14	54	26
TVA 1747	<1	<1	6	65	29
TVA 8902	<1	16	24	56	4
Avg.	<1	6	13	59	23
S.D.[c]	<1	7	11	5	13
C.V.(%)[d]	<1	117	85	8	57

---

[a] The percentages in Appendices F-5 to F-9 were summed by hydrocarbon group and in total. The group sum was then divided by the total to obtain the data for this table.

[b] No data

[c] S.D. = standard deviation

[d] C.V. = coefficient of variation

[e] Insufficient data to calculate standard deviation and coefficient of variation.

TABLE 13 (CONT'D). PERCENTAGE OF EACH HYDROCARBON GROUP TO TOTAL DETAILED HYDROCARBONS[a]

Hot Purge Cycle

Gasoline

Canister Number	40	41-55	56-72	73-84	85-99
DOE 201	<1	25	44	31	<1
DOE 202	<1	30	43	26	1
DOE 205	1	14	23	47	14
DOE 206	8	39	29	19	4
Avg.	2	27	35	31	5
S.D.[c]	4	10	10	12	6
C.V.(%)[d]	200	37	29	39	120
EPA A1480008	4	57	22	16	<1
EPA A1480049	1	27	32	37	4
EPA A1480073	2	37	34	26	1
EPA A1480039	<1	31	23	38	8
EPA A1480060	4	36	20	33	7
Avg.	2	38	26	30	4
S.D.[c]	2	12	6	9	4
C.V.(%)[d]	100	32	23	30	100

Blend

Canister Number	< 40	41-55	56-72	73-84	85-99
DOE 101	<1	24	36	39	1
DOE 102	<1	26	41	27	6
DOE 104	<1	15	26	47	12
DOE 106	--[b]	--	--	--	--
Avg.	<1	22	34	38	6
S.D.[c]	<1	6	8	10	6
C.V.(%)[d]	<1	27	24	26	100
EPA A1480096	<1	35	23	31	11

---

[a] The percentages in Appendices were summed by hydrocarbon group and in total. The group sum was then divided by the total to obtain the data for this table.

[b] No Data

[c] S.D. = standard deviation

[d] C.V. = coefficient of variation

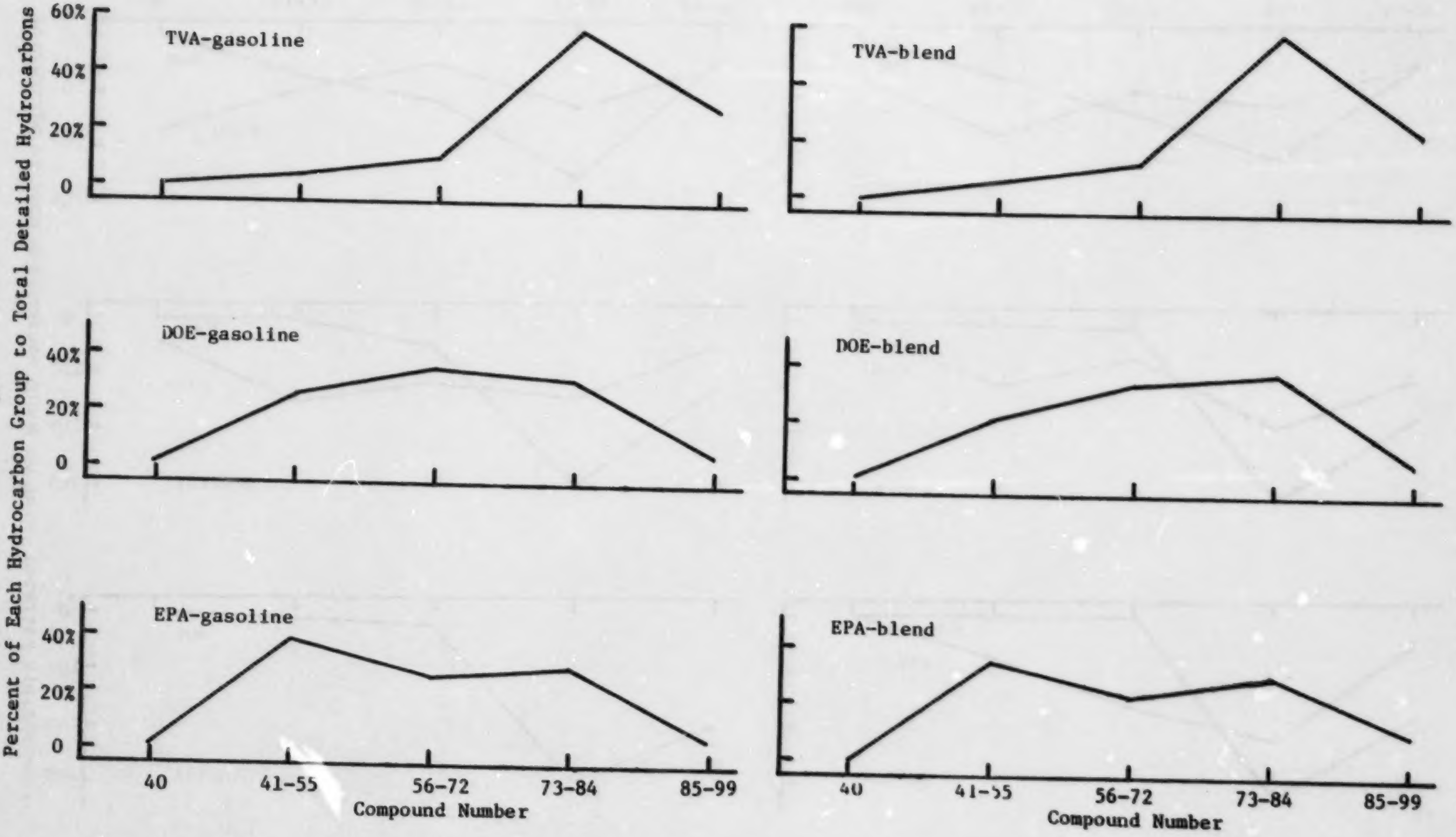


Figure 5. Comparison of the distribution of detailed hydrocarbon emissions from hot purge cycles averaged by fleet and by fuel type

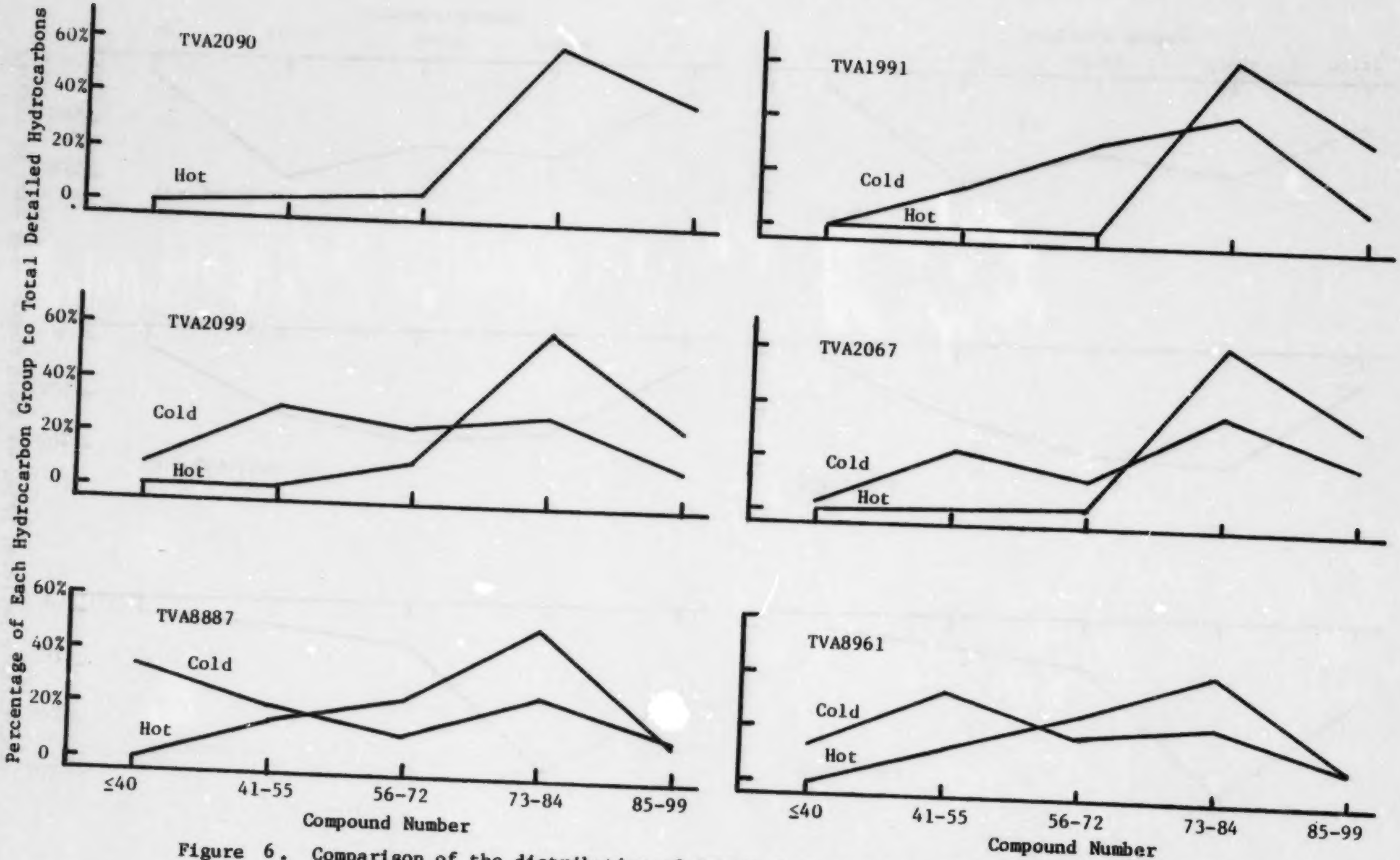


Figure 6. Comparison of the distribution of detailed hydrocarbon emissions sampled from TVA charcoal samples during cold and hot purge cycles

2067, and 8961. The peaks occurred in the C_7 to C_8 and the C_9 category. It is difficult to discern any meaningful difference between the hydrocarbon distributions of the gasoline charcoals (2090, 2099, and 8887) and the blend charcoals (1991, 2067, and 8961).

A comparison of detailed hydrocarbon emissions was also made for the sum of cold and hot purge tests for TVA canisters. These results are reported in Table 14. The percentage of each hydrocarbon group to total hydrocarbons was summed for cold and hot purges. The group sum was then divided by the total (of both cold and hot purges) to obtain data for this table. The resulting group values for each canister typically fell between the individual cold and hot purge values.

TABLE 14. PERCENTAGE OF EACH HYDROCARBON GROUP TO TOTAL DETAILED HYDROCARBONS FROM COLD AND HOT PURGE CYCLES OF TVA CHARCOALS[a]

Fuel Type	Canister Number		40	41-55	56-72	73-84	85-99
Gasoline	2090		--[b]	--	--	--	--
	2099		0	15	13	57	15
	8887		15	12	18	45	9
		Avg.	8	14	16	51	12
		S.D.[c]	--[e]	--	--	--	--
		C.V.(%)[d]	--[e]	--	--	--	--
Blend	1991		0	0	5	63	32
	2067		0	3	7	57	33
	8961		6	21	26	40	7
		Avg.	2	8	13	55	25
		S.D.[c]	4	11	11	13	15
		C.V.(%)[d]	173	142	87	23	61

---

[a] The percentages in Appendices F-5 and F-6 were summed for cold and hot purge by hydrocarbon group and in total. The group sum was then divided by the total to obtain data for this table.

[b] No data

[c] S.D. = Standard deviation

[d] C.V. = Coefficient of variation

[e] Insufficient data to calculate standard deviation and coefficient of variation

The hydrocarbon speciation data were subdivided into percent paraffins, olefins, and aromatics for each charcoal sample. The data are given in Appendix G and are summarized in Table 15. Peak areas which included a mixture of paraffins, olefins, and/or aromatics, were omitted from the calculations. Actual distribution of the compounds could differ as a result of these unresolved peaks.

TABLE 15. SUMMARY OF PERCENTAGES OF PARAFFINS, OLEFINS AND AROMATICS IN PURGED CHARCOAL EFFLUENT FROM 50 g SAMPLES FROM IN-USE EVAPORATIVE CANISTERS[a]

Canister Fleet	Purge Cycle	Paraffins	Olefins	Aromatics
TVA	Cold	53	7	39
TVA	Hot	36	1	63
DOE	Hot	66	0	34
EPA	Hot	64	1	35

The hot purged effluent of TVA charcoals was on average, composed of a predominance of aromatics (63 percent) over paraffins (36 percent), while hot purged DOE and EPA charcoals produced more paraffins (66 and 64 percent, respectively) than aromatics (34 and 35 percent). The relatively large difference in proportions of paraffins and aromatics between canister fleets could be related to differences in the compositions of fuels used for each fleet. The cold purge cycle of TVA charcoals produced, on average, higher fractions of paraffins and olefins than hot purged TVA charcoal samples, but a lower percentage of aromatics.

G. Summary of Results

The emissions data measured in this program have been analyzed to determine relationships to several variables. The data have been compared by fleet, fuel type, vehicle class, and type of purge cycle (cold or hot). Comparing the data by groups was in most cases not statistically valid because overlap occurred for most data groupings at the 95 percent confidence level. Relative comparisons were made, however.

- The TVA fleet of canisters (gasoline and blend) produced higher levels of water and total hydrocarbons and had higher working capacities than canisters from the DOE or EPA fleets. The TVA canisters (gasoline and blend) produced higher levels of total alcohols than the DOE canisters. These higher values were apparently due to the Chevy Chevette canisters. EPA gasoline canisters had average water content, total hydrocarbon levels, and working capacities that were similar to but slightly lower than those from the DOE canisters. It is difficult to interpret the differences observed between fleets (TVA, DOE, EPA) due to vehicle operation characteristics which likely varied between fleets. The length of time a vehicle sits between trips, the speed at which a vehicle is operated, the vapor pressure of the fuel, and ambient temperature are a few of the variables that will affect the type of vapors to which an evaporative canister is exposed.

- Only small differences in water content, total hydrocarbon levels, and working capacities were discerned between gasoline and blend canisters.

- Alcohols were produced by both gasoline and blend fueled vehicle canisters. Roughly equivalent levels of total alcohols were produced by TVA gasoline and blend charcoals, however, DOE blend charcoals produced approximately four times the quantity of alcohols emitted by DOE gasoline charcoals. Total alcohol content did not appear to correlate with water content, total hydrocarbons, or working capacity.

- Hot purge water, total hydrocarbon, and total alcohol emissions were generally higher than cold purge emissions for TVA gasoline and blend charcoal samples.

- TVA canisters produced a higher proportion of heavier hot purge detailed hydrocarbons than DOE or EPA canisters. DOE hot purge hydrocarbons were evenly distributed between light and heavy ends. The hydrocarbon distribution from hot purged EPA charcoal was identified by an "M" shaped distribution curve which was proportionally higher in C_7 and C_8 compounds and in C_9 compounds.

- TVA canisters contained more unsaturated hydrocarbons than DOE and EPA canisters.

- There was no observable difference in the hydrocarbon distribution from gasoline and blend canisters.

- Cold purge detailed hydrocarbons were predominantly in the C_3 to C_8 range and hot purge hydrocarbons in the C_9 to C_{11} range.

- Total recovered weight (sum of weights of water, alcohols, and total hydrocarbons) typically exceeded charcoal weight loss (determined by weighing before and after purging). Total recovered and charcoal weight loss agreed within 15% for all DOE and EPA canisters, but for less than half of the TVA canisters. The disparity between TVA weight losses could be due to a greater proportion of unsaturated compounds in the TVA charcoal effluent.

- Hot purge charcoal weight loss typically exceeded cold purge charcoal weight loss for each fleet.

V. QUALITY ASSURANCE

The Quality Assurance (QA) guidelines addressed in the QA Project Plan were followed in performing the work for this program. Calibrations were performed on the analytical instruments and daily sampling system leak checks were conducted. The data is available for inspection if desired. Precision, accuracy,and completeness figures determined for this program are summarized in Table 16.

TABLE 16. PRECISION, ACCURACY, AND COMPLETENESS

Measurement	Analytical Procedure	Precision Std. Dev.[a]	Accuracy, %	Completeness, %
Methanol	Gas Chromatograph (FID)	2[b]	91[c]	>95
Ethanol	Gas Chromatograph (FID)	4[b]	94[c]	>95
TBA	Gas Chromatograph (FID)	2[b]	85[c]	>95
Water Content	Gravimetric	0.00	105[c]	>95
THC	Gas Chromatograph (FID)	0.04	70[c]	>95
Selected HC Speciation	Gas Chromatograph (FID)	10[b]	70[d]	>93

---

[a] Standard deviation except where indicated

[b] Coefficient of variation

[c] Based on recovery experiments conducted on the sampling system

[d] Recovery is the same as that for the THC, however the recoveries of individual HC species will vary. It was not within the scope of this program to determine the recovery of each component in the gasoline spike.

Preceding page blank

REFERENCES

1. Code of Federal Regulations, Title 40, Chapter 1, Part 85, Subpart H, Sections application to Light-Duty Vehicles.
2. Unpublished data from EPA-RTP report.
3. Procedures provided to EPA by Ford and ARCO.
4. Warner-Selph, Mary Ann, "The Effect of Methanol on Evaporative Canister Charcoal Capacity," Final Report to the Environmental Protection Agency prepared under Contract No. 68-03-3162, Work Assignment 12, Report No. EPA 460/3-84-014, January 1985.

Preceding page blank

APPENDIX A

BUTANE WORKING CAPACITY PROCEDURE

APPENDIX A

BUTANE WORKING CAPACITY PROCEDURE

Following the "room temperature" purge to a stable weight, conduct a butane working capacity test on the canister as follows:

1. Record the initial canister weight.
2. Load the canister with butane until breakthrough occurs (1000 ppmC), and record the time to breakthrough.
3. Record the loaded canister weight.
4. Purge the canister with room temperature air[a] at the same flow rate as the previous purge until the weight stabilizes to within one gram over an hour, and record the elapsed time and final weight. The loaded weight minus the final weight is the working capacity.
5. Repeat steps 1 to 4.
6. If the difference between the two working capacities as measured above is greater than 10% of the higher value, repeat steps 1 to 4 again.

On the cansiters that underwent speciation of their initial room temperature purge, speciation shall also be done on the vapors from the butane working capacity purge to see what other compounds, if any, are desorbed along with the butane. Then the high temperature purge and speciation would be conducted as planned on all the canisters being tested.

---

[a] Dry nitrogen was used instead of room air to minimize the possibility of adding water to the charcoal. Per what was found in the mini-canister work, the use of dry nitrogen probably yielded greater working capacities than would have been found with room air.(4)

APPENDIX B

THE MEASUREMENT OF METHANOL, ETHANOL, AND TERTIARY BUTYL ALCOHOL IN EXHAUST

APPENDIX B

THE MEASUREMENT OF METHANOL,ETHANOL, AND TERTIARY BUTYL ALCOHOL IN EXHAUST

The measurement of methanol, ethanol, and tertiary butyl alcohol (TBA) in exhaust is accomplished by bubbling the exhaust through glass impingers containing deionized water. The exhaust sample is collected continuously during the test cycle. For analysis, a portion of the aqueous solution is injected into a gas chromatograph equipped with a flame ionization detector (FID). External methanol, ethanol, and TBA standards in deionized water are used to quantify the results. Detection limits for this procedure are on the order of 0.06 ppm in dilute exhaust for both methanol and ethanol.

SAMPLING SYSTEM

Two glass impingers in series, with each containing 25 mℓ of deionized water are used to collect exhaust samples for the analysis of methanol, ethanol, and TBA. A flow schematic of the sample collection system is shown in Figure 1. The two glass impingers collect 99+ percent each of methanol and ethanol, and 99 percent of TBA in exhaust. The temperature of the impingers are maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/minute by a sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. The Teflon line connecting the CVS and the solenoid valve is heated to ∿175°F in order to prevent water from condensing in the sample line. Several views of the sampling system are shown in Figure 2.

ANALYTICAL PROCEDURE

The analysis of methanol, ethanol, and TBA is accomplished by collecting the alcohols in deionized water and analyzing the sample with a gas chromatograph equipped with an FID. The analysis flow schematic for methanol, ethanol, and TBA is shown in Figure 3. A detailed description of the procedure follows.

For the analysis of the three alcohols, dilute exhaust is bubbled through two glass impingers each containing 25 mℓ of deionized water. Upon completion of each driving cycle, the impinger is removed and the contents are transferred to a 30 mℓ polyethylene bottle, and capped.

A Perkin-Elmer 3920B gas chromatograph equipped with a flame ionization detector is used to analyze the sample. A 5 μℓ portion of the sample is injected into the gas chromatograph (GC). The analytical

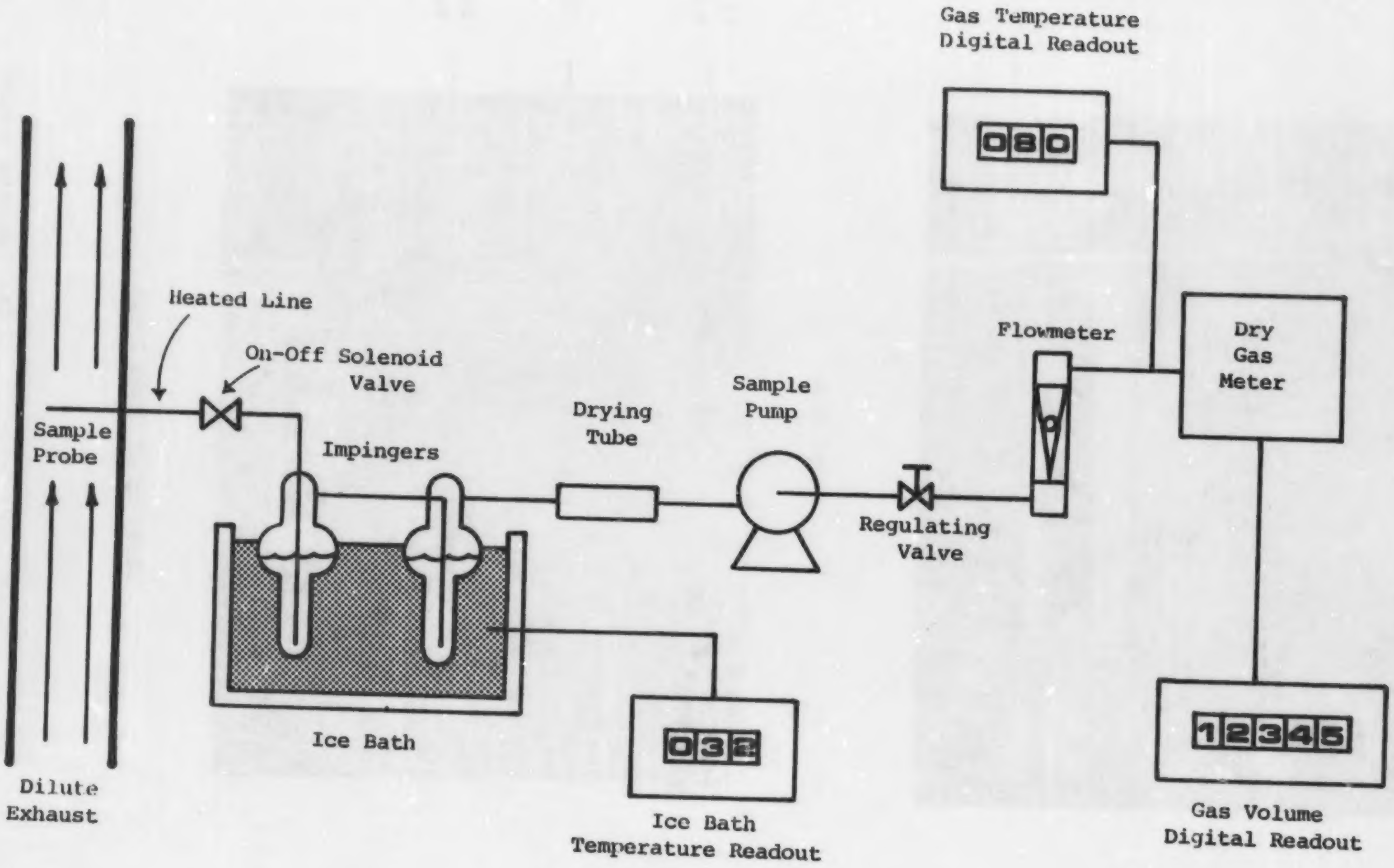
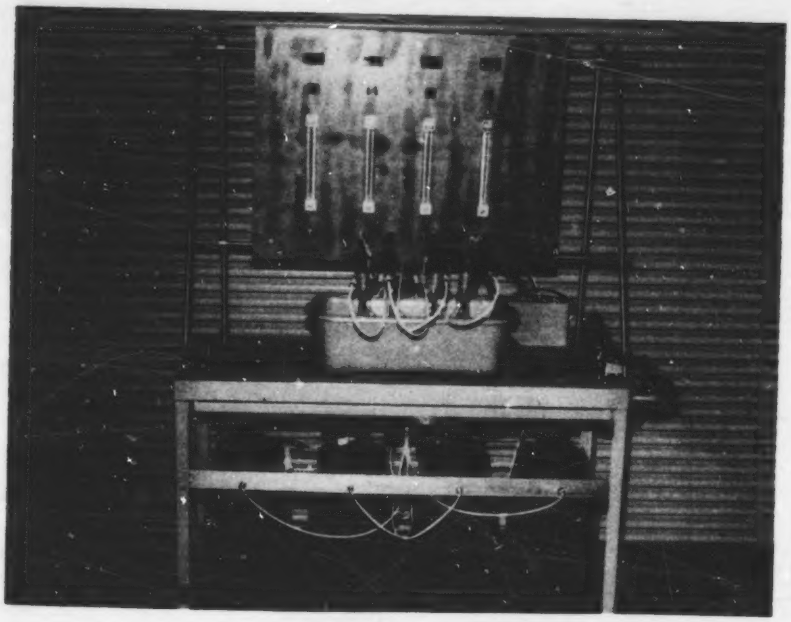
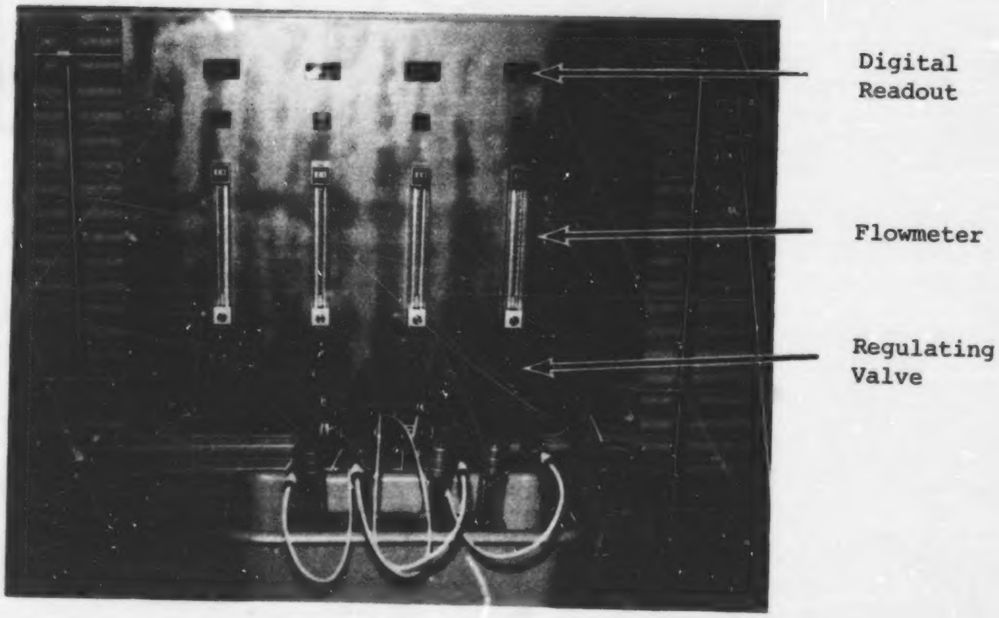

Gas Temperature Digital Readout
080
Heated Line
On-Off Solenoid Valve
Sample Probe
Impingers
Drying Tube
Sample Pump
Flowmeter
Dry Gas Meter
Regulating Valve
Ice Bath
032
Dilute Exhaust
Ice Bath Temperature Readout
12345
Gas Volume Digital Readout

Figure 1. Methanol, ethanol, and TBA sample collection flow schematic

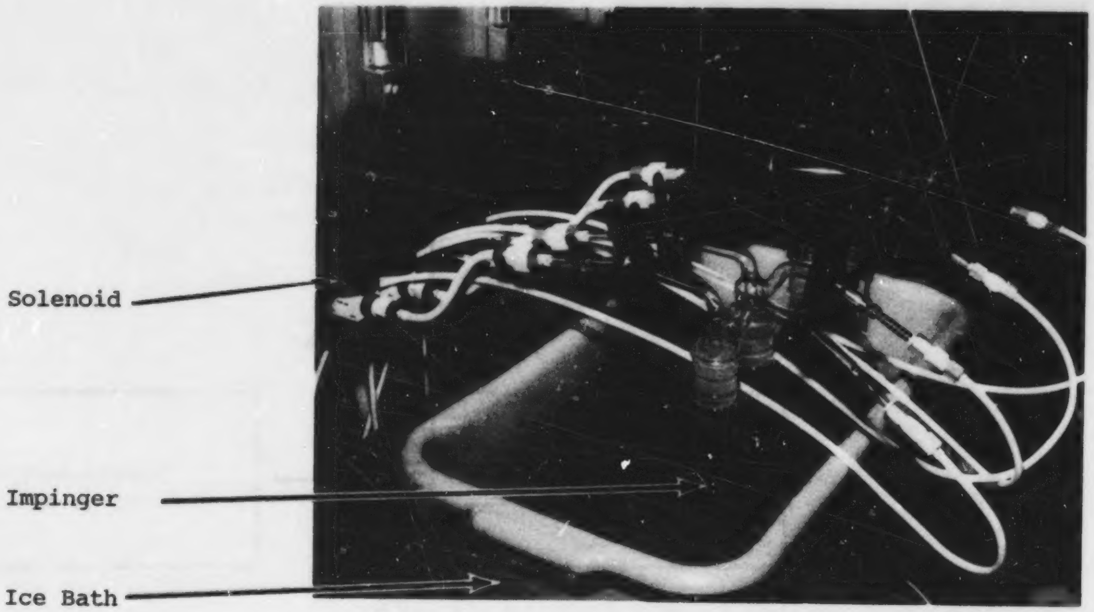


Front View

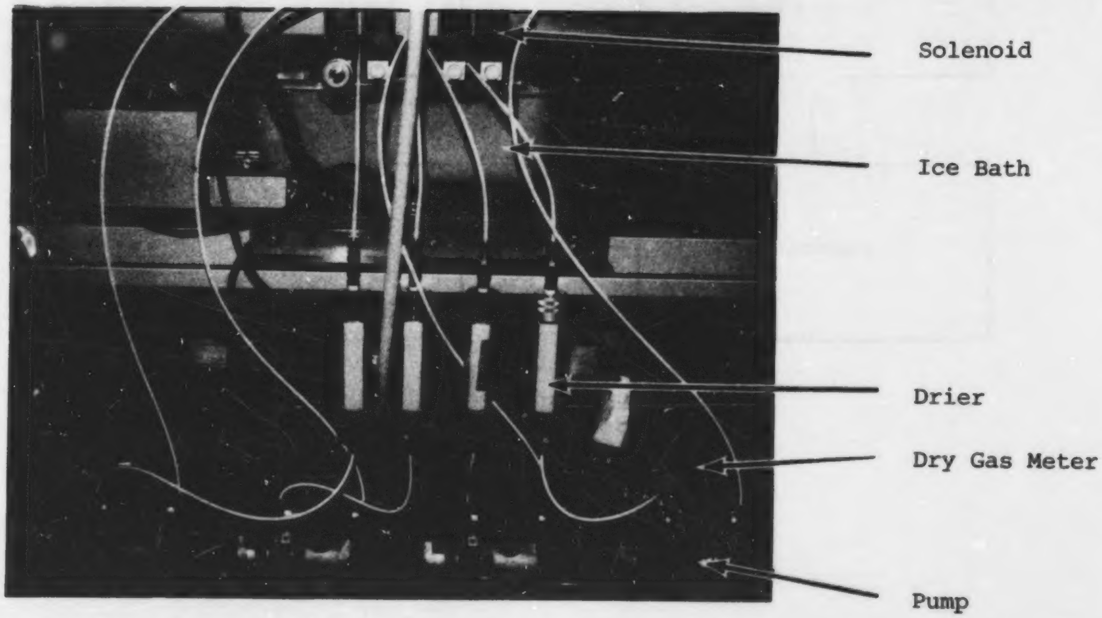

Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. Methanol, ethanol, and TBA sampling system

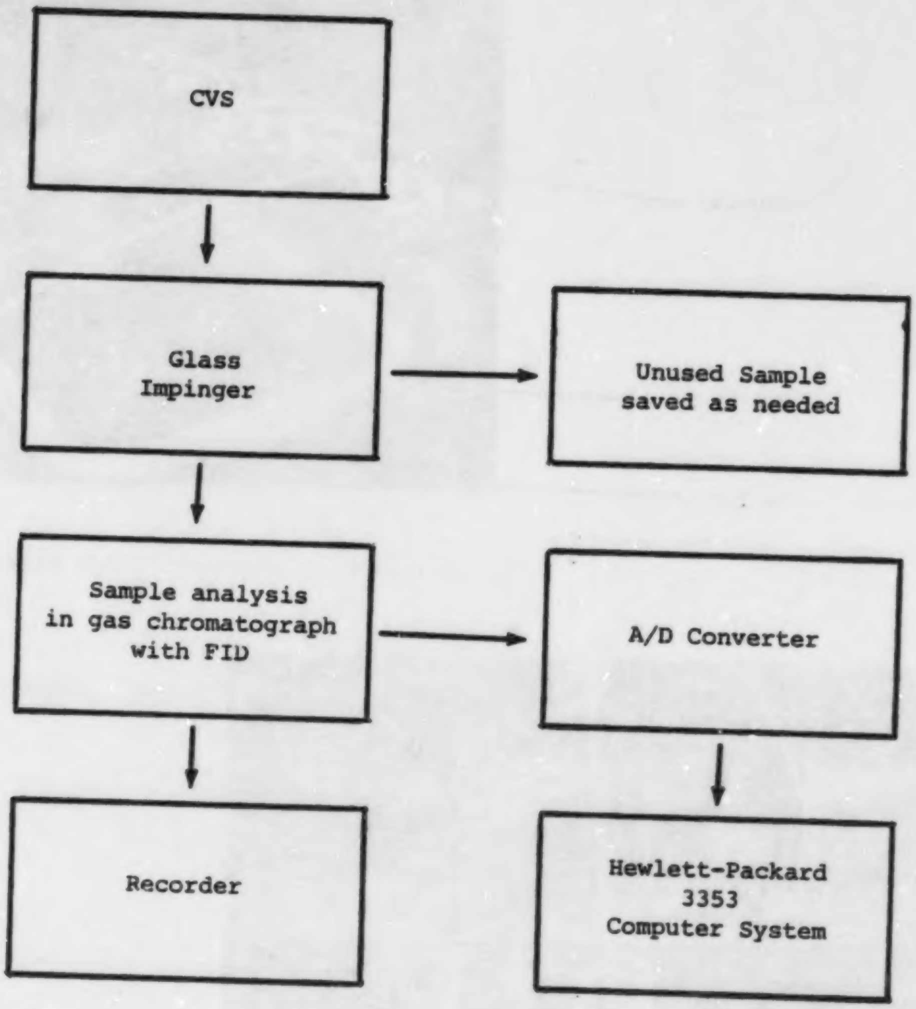

Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). Methanol, ethanol, and TBA sampling system



CVS
Glass Impinger
Unused Sample saved as needed
Sample analysis in gas chromatograph with FID
A/D Converter
Recorder
Hewlett-Packard 3353 Computer System

Figure 3. Methanol, ethanol, and TBA analysis flow schematic

column is a 3' x 1/8" Teflon column containing 120/150 mesh Porapak Q. The carrier gas which is helium, flows through the column at a rate of 20 mℓ/minute. The column temperature is maintained at approximately 105°C for methanol, 140°C for ethanol, and 150°C for TBA analyses. A 79.1 ppm methanol standard is shown in Figure 4, a 78.9 ppm ethanol standard is shown in Figure 5, and a 78.9 ppm TBA standard is shown in Figure 6.

To quantify the results, the sample peak areas are compared to the peak areas of standard solutions. Figure 7 shows the analytical system with gas chromatograph, detector, A/D converter, and recorder.

CALCULATIONS

The procedure has been developed to provide the user with the concentration of methanol, ethanol, and TBA in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm. The equations for determining the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92"Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}(\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg}}$$

The next step converts the volume from cubic feet to cubic meters by use of the conversion factor: 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr(m^3)} = \frac{P_{exp}(\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

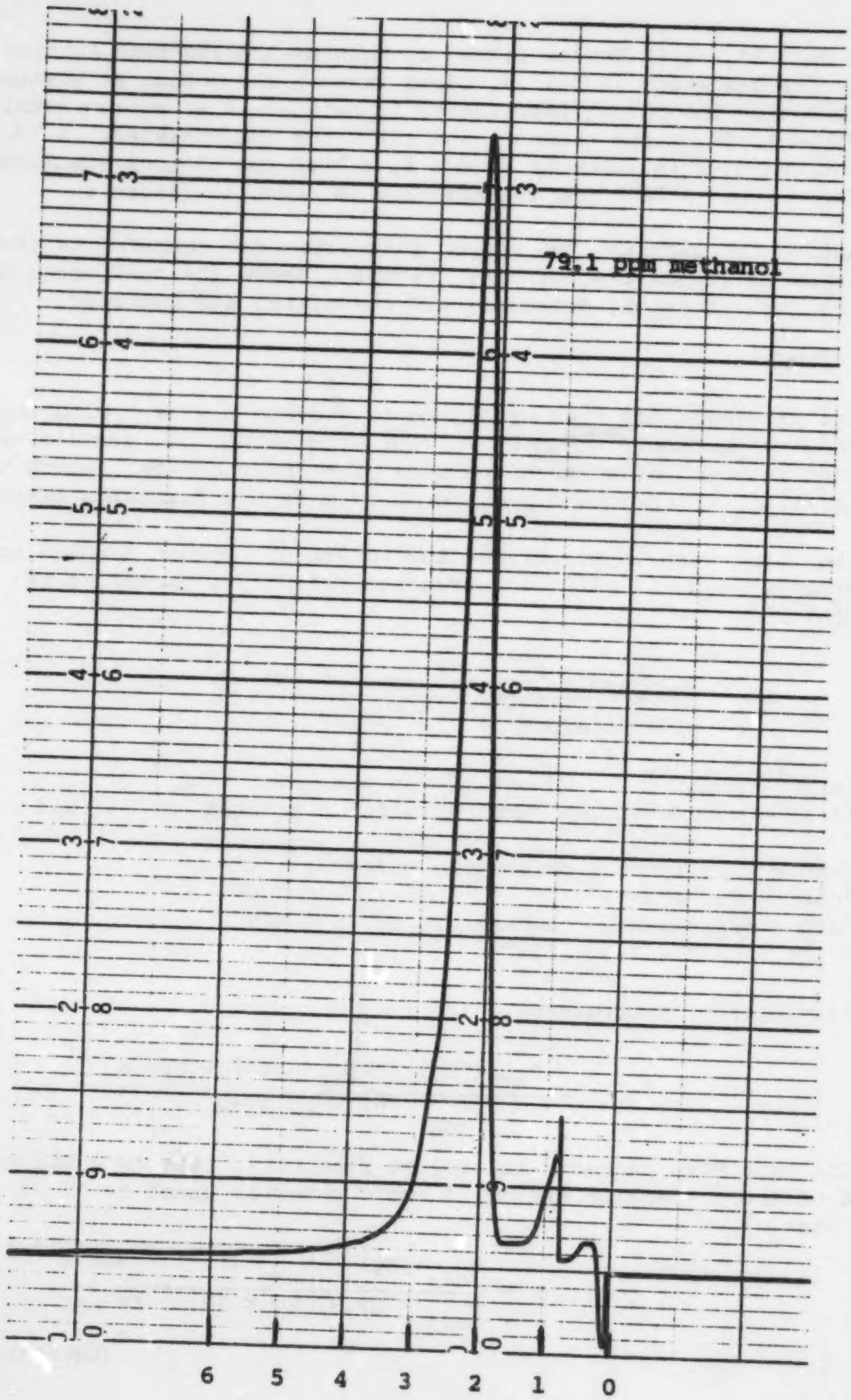


Figure 4. Chromatogram of methanol standard

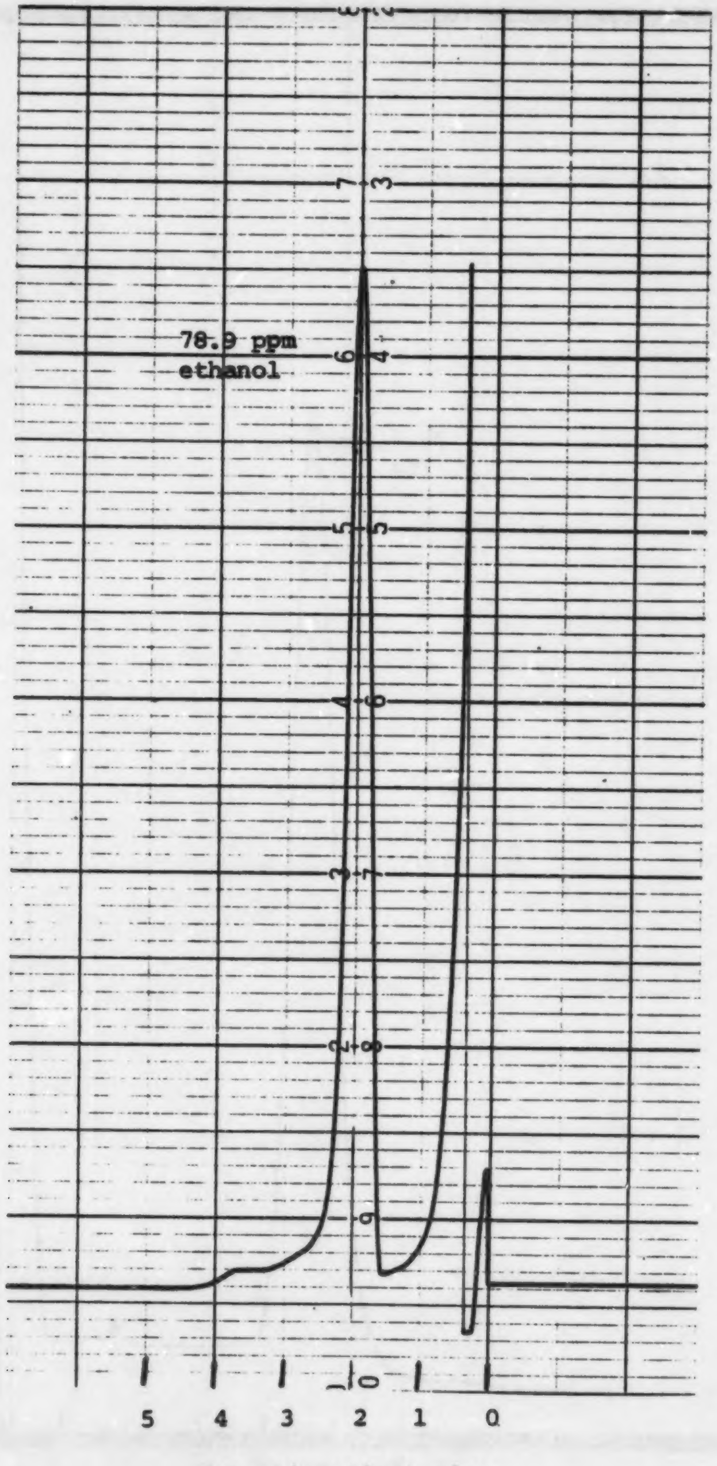


Figure 5. Chromotogram of ethanol standard

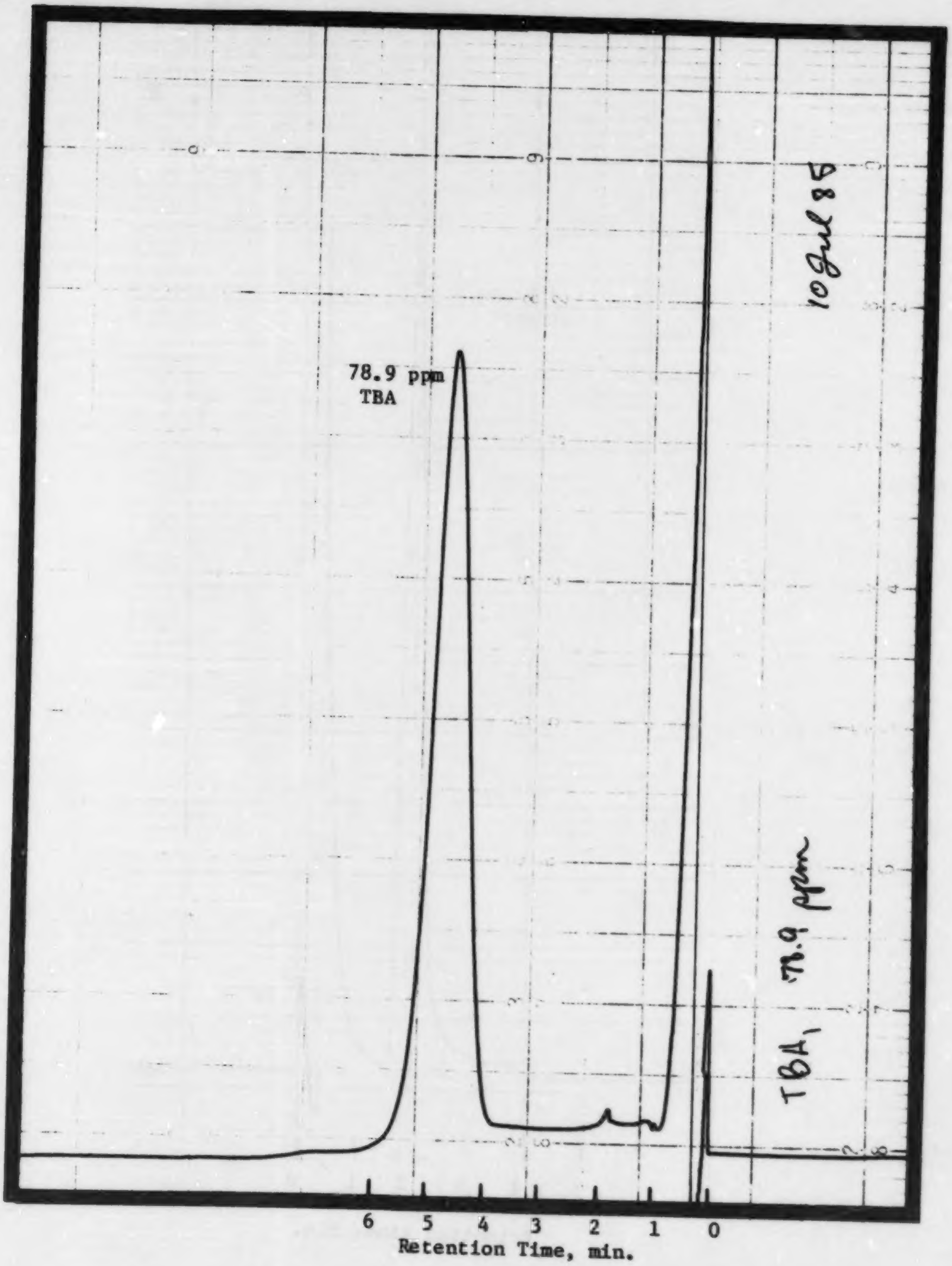


Figure 6. Chromatogram of TBA standard

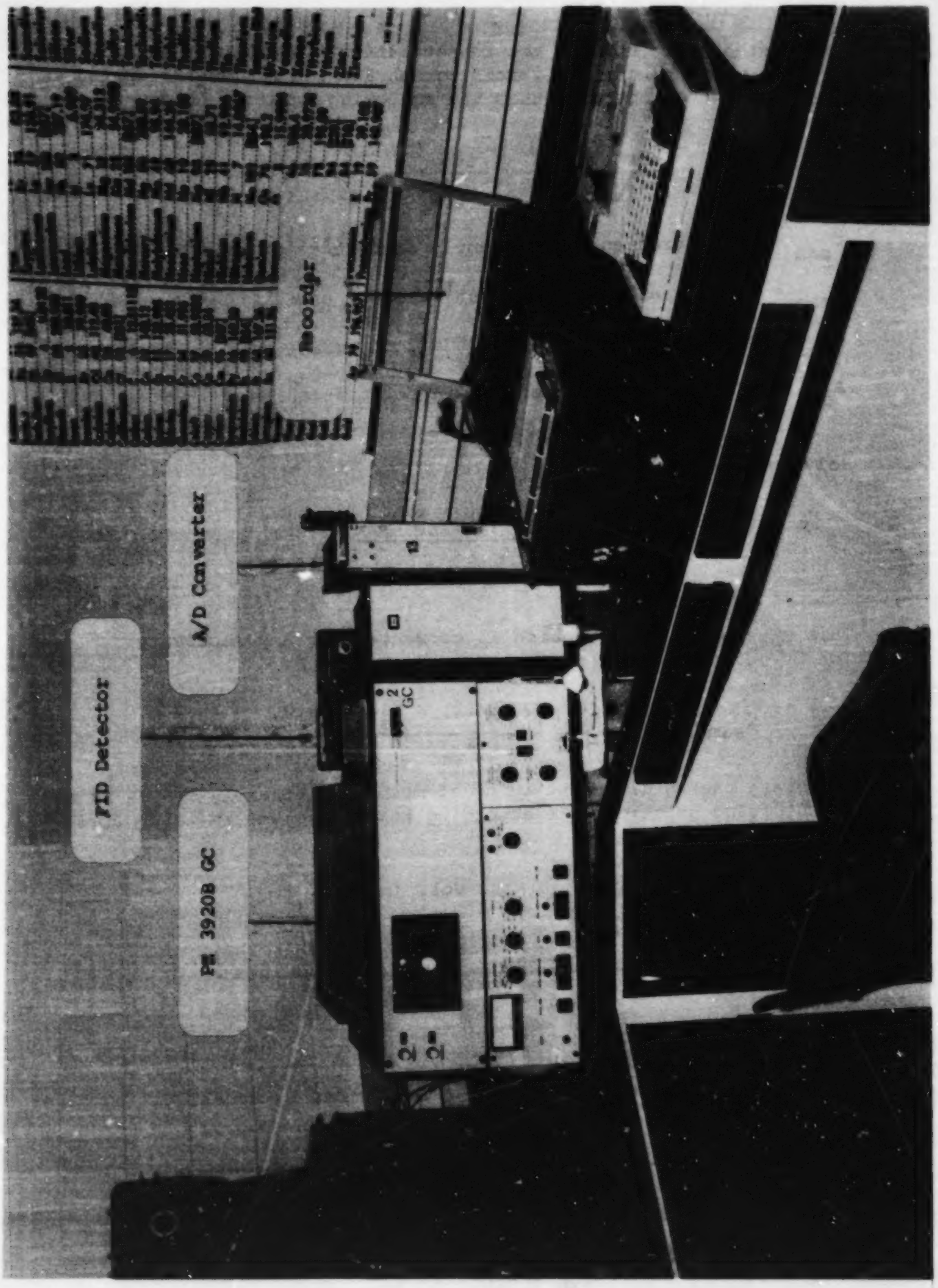

Recorder
A/D Converter
FID Detector
PE 3920B GC

Figure 7. Analytical system

The next step is to find the concentration of methanol, ethanol, or TBA in μg/mℓ. Since the gas chromatograph FID has a linear response in the concentration of concern, then the following equation holds.

$$\frac{C_{sam}\ (\mu g/m\ell)}{A_{sam}} = \frac{C_{std}\ (\mu g/m\ell)}{A_{std}}$$

C_{sam} = concentration of the sample in μg/mℓ

A_{sam} = GC peak area of sample in relative units

C_{std} = concentration of the standard in μg/mℓ

A_{std} = GC peak area of standard in relative units

Solving for C_{sam} gives:

$$C_{sam(\mu g/m\ell)} = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam}}{A_{std}}$$

This C_{sam} (μg/mℓ) in solution is corrected for any necessary dilution by multiplying by the dilution factor, D.F.

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.}}{A_{std}}$$

To obtain the total amount in μg of methanol, ethanol, or TBA in the aqueous absorbing solution, the absorbing reagent volume is multiplied by the concentration to give:

$$\mu g\ \text{sample} = C_{sam}\ (\mu g/m\ell) \times \text{Abs. Vol. } (m\ell)$$

$$= \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{A_{std}}$$

(Equation 2)

To obtain μg sample/m^3, Equation 2 is divided by Equation 1 to give:

$$\mu g\ \text{samp}/m^3 = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg}) \times 528^\circ}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ (ft^3/m^3)}{V_{exp}\ (ft^3)}$$

(Equation 3)

To find the concentration of methanol, ethanol, or TBA in ppm, the density of each alcohol is needed. At 29.92"Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_1}{T_1}$$

$V_1 = 22.4\ell$
$T_1 = 32^\circ F + 460 = 492^\circ R$
V = volume at 68°F
$T = 68^\circ F + 460 = 528^\circ R$

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 24.04ℓ at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 24.04 ℓ/mole

$$\text{den } (g/\ell) = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}}$$

The density in μg/mℓ can be found by converting g to μg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}} \times \frac{1 \times 10^6 \mu g/g}{1 \times 10^3 m\ell/\ell} = \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration in ppm, the concentration in μg/m³ is divided by the density in μg/mℓ

$$\text{ppm} = \mu g/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$\text{ppm} = \frac{24.04(\ell) \times C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{\text{Mol. Wt. (g/mole)} \times 1000 \times A_{std} \times P_{exp}\ (\text{"Hg})}$$

$$\times \frac{T_{exp}(^\circ R) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528^\circ R \times V_{exp}\ (ft^3)}$$

(Equation 5)

At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 3) and ppm (Equation 5) at 68°F and 29.92"Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period, a Hewlett-Packard 67 program was developed to calculate the methanol, ethanol, and TBA concentrations in $\mu g/m^3$ and ppm from the raw data. This program is presented in Figure 8.

Sample Calculation

Assume exhaust samples were collected in glass impingers for cold and hot UDDS segments of a four-bag FTP. Raw data for these tests are presented in Figure 9. Calculations were performed using the HP-67 program and manual calculations.

Manual calculations for the cold start UDDS segment of the FTP

For Bubbler #1 - Methanol

$$\mu g/m^3 CH_3OH = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg})}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528^\circ R \times V_{exp}\ (ft^3)}$$

$$= \frac{(79.1\ \mu g/m\ell) \times 10{,}000 \times 1 \times 25}{20{,}000 \times 29.80\text{"Hg}}$$

$$\times \frac{(460 + 75) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528^\circ R \times 3.196\ ft^3}$$

$$= 1.11 \times 10^4\ \mu g/m^3$$

The concentration of methanol in Bubbler #2 is calculated in the same manner using the appropriate dilution factor, standard concentration, standard area, and sample area:

For Bubbler #2:

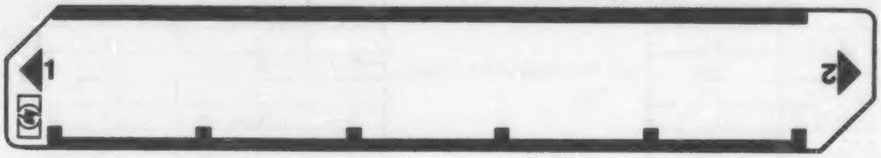
$$\mu g/m^3 = \frac{7.91\ \mu g/m\ell \times 10{,}000 \times 1 \times 25}{25{,}000 \times 29.80}$$

$$\times \frac{(460 + 75) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528^\circ R \times 3.196\ ft^3}$$

$$= 8.89 \times 10^2\ \mu g/m^3$$

Figure 8. HP-67

User Instructions



STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; switch to run				
0_2	Feed side 1 of card in from right to left				
0_3	Set decimal place		g	Sci	
1	Input Sample Volume	ft^3	A		
2	Input Barometric Pressure	"Hg	R/S		
3	Input Sample Temperature	°F	R/S		
4	Input Absorbing Reagent Volume	mℓ	R/S		
5	Input Dilution Factor, Bubbler #1		R/S		
6	Input Methanol Standard Conc. Bubbler #1	μg/mℓ	R/S		
7	Input Methanol Standard Area, Bubbler #1	counts	R/S		
8	Input Methanol Sample Area, Bubbler #1	counts	R/S		
9	Output Methanol Sample Conc., Bubbler #1				$\mu g/m^3$
10	Input Dilution Factor, Bubbler #2		R/S		
11	Input Methanol Standard Conc., Bubbler #2	μg/mℓ	R/S		
12	Input Methanol Standard Area, Bubbler #2	counts	R/S		
13	Input Methanol Sample Area, Bubbler #2	counts	R/S		
14	Output Methanol Sample Conc., Bubbler #2		R/S		$\mu g/m^3$
15	Output Methanol Sample Conc., Bubbler #1 & #2		R/S		$\mu g/m^3$
16	Output Methanol Sample Conc.				ppm
17	Input Ethanol Standard Conc., Bubbler #1	μg/mℓ	R/S		
18	Input Ethanol Standard Area, Bubbler #1	counts	R/S		
19	Input Ethanol Sample Area, Bubbler #1	counts	R/S		
20	Output Ethanol Sample Conc., Bubbler #1				$\mu g/m^3$
21	Input Ethanol Standard Conc., Bubbler #2	μg/mℓ	R/S		
22	Input Ethanol Standard Area, Bubbler #2	counts	R/S		
23	Input Ethanol Sample Area, Bubbler #2	counts	R/S		
24	Output Ethanol Sample Conc., Bubbler #2		R/S		$\mu g/m^3$
25	Output Ethanol Sample Conc., Bubbler #1 & #2		R/S		$\mu g/m^3$
26	Output Ethanol Sample Conc.				ppm
27	Input TBA Standard Conc., Bubbler #1	μg/mℓ	R/S		
28	Input TBA Standard Area, Bubbler #1	counts	R/S		
29	Input TBA Sample Area, Bubbler #1	counts	R/S		
30	Output TBA Sample Conc., Bubbler #1				$\mu g/m^3$
31	Input TBA Standard Conc., Bubbler #2	μg/mℓ	R/S		
32	Input TBA Standard Area, Bubbler #3	counts	R/S		
33	Input TBA Sample Area, Bubbler #2	counts	R/S		
34	Output TBA Sample Conc., Bubbler #2		R/S		$\mu g/m^3$
35	Output TBA Sample Conc., Bubbler #1 & #2		R/S		$\mu g/m^3$
36	Output TBA Sample Conc.				ppm
			h	RTN	

Figure 8 (cont'd). HP-67 Program Form

STEP	KEY ENTRY	KEY CODE	COMMENTS	STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	In sample Vol, ft³		R/S	84	Out Ethanol Sample Conc, Bub#1, µg/m³
	2	02			RCL 5	34 05	In Std. Ethanol Conc, µg/mℓ
	÷	81			X	71	
	R/S	84	In Barometric Pres. "Hg	060	R/S	84	In Std. Ethanol Area
	X	71			÷	81	
	STO 1	33 01			R/S	84	In Ethanol Sample Area, Bub#2
	R/S	84	In Sample Temp, F°		X	71	
	4	04			R/S	84	Out Ethanol Conc., Bub.#2, µg/m³
	6	06			RCL 6	34 06	
010	0	00			+	61	
	+	61			R/S	84	Out Ethanol Conc., µg/m³
	RCL 1	34 01			1	01	
	÷	81			9	09	
	R/S	84	In Sol.Vol., mℓ	070	1	01	
	X	71			6	06	
	STO 2	33 02			÷	81	
	RCL 2	34 02			R/S	84	Out Ethanol Conc., ppm
	R/S	84	In Dilution Factor		RCL 3	34 03	In Std TBA Conc., µg/mℓ
	X	71			X	71	
020	STO 3	33 03			R/S	84	In Std TBA Area
	RCL 3	34 03			÷	81	
	R/S	84	In Std.Methanol Conc, µg/mℓ		R/S	84	In TBA Sample Area, Bub #1
	X	71			X	71	
	R/S	84	In Std Methanol Area	080	STO 7	33 07	
	÷	81			R/S	84	Out TBA Sample Conc, Bub #1, µg/m³
	R/S	84	In Methanol Sample Area, Bub#1		RCL 5	34 05	
	X	71			X	71	
	STO 4	33 04			R/S	84	In Std TBA Conc. µg/mℓ
	R/S	84	Out Methanol Sample Conc, Bub#1 µg/m³		÷	81	In Std TBA Area
030	RCL 2	34 02			R/S	84	In TBA Sample Area, Bub #2
	X	71	In Dilution Factor		X	71	
	STO 5	33 05			R/S	84	Out TBA Conc., µg/m³
	RCL 5	34 05			RCL 7	34 07	
	R/S	84	In Std. Methanol Conc, µg/mℓ	090	+	61	
	X	71			R/S	84	
	R/S	84	In Std. Methanol Area		3	03	
	÷	81			0	00	
	R/S	84	In Methanol Sam. Area, Bub#2		8	08	
	X	71			3	03	
040	R/S	84	Out Methanol Sam. Conc, Bub#2, µg/m³		÷	81	
	RCL 4	34 04			R/S	84	Out TBA Conc., ppm
	+	61			h RTN	35 22	
	R/S	84	Out Methanol Conc, µg/m³				
	1	01		100			
	3	03					
	3	03					
	3	03					
	÷	81					
	R/S	84	Out ppm Methanol				
050	RCL 3	34 03	In Std Ethanol Conc, µg/mℓ				
	X	71					
	R/S	84	In Std. Ethanol Area				
	÷	81					
	R/S	84	In Ethanol Sam. Area Bub#1	110			
	X	71					
	STO 6	33 06					

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C	D	E	I

SWRI PROJECT NO.__________TEST NO.__________TEST DATE:__________VEHICLE:__________

FUEL:_______CVS NO._______TUNNEL SIZE:________DRIVER:__________MILES:__________

SAMPLE COLLECTION BY:__________CHEMICAL ANALYSIS BY:_______CALCULATIONS BY:________

GENERAL COMMENTS:____

Test No.	1	2	3	4	5	6
Driving Cycle	CS-FTP	HS-FTP	HFET	SET-7	30 mph	Bckgrnd.
Volume, $Ft.^3$	3.196	3.207	2.010	3.730	1.625	8.241
B.P., "Hg	29.80	29.50	29.02	29.25	30.02	29.95
Temp. °F	75	85	96	85	80	83
Absor. Rea. Vol., mℓ	25	75	50	50	25	75
Dilution Factor, Bubbler #1	1	1	10	2	5	1
Std. Conc. μg CH_3OH/mℓ Bub.#1	79.1	0.791	791.	7.91	79.1	7.91
Std. Area - Bubbler #1	20000	1000	10000	1000	5000	5000
Sample Area - Bubbler #1	10000	3000	1000	3000	1000	15000
Sam. Conc. μg CH_3OH/m^3, Bub#1	$1.11\mathrm{X}10^{4}$	$2.05\mathrm{X}10^{3}$	$7.54\mathrm{X}10^{5}$	$2.37\mathrm{X}10^{5}$	$2.37\mathrm{X}10^{4}$	$7.83\mathrm{X}10^{3}$
Dilution Factor, Bubbler #2	1	1	5	1	2	1
Std. Conc.μg CH_3OH/mℓ Bub.#2	7.91	0.791	7.91	0.791	7.91	0.791
Std. Area - Bubbler #2	25000	5000	5000	1000	1500	6000
Sample Area - Bubbler #2	10000	15000	6000	100	300	1000
Sam. Conc. μgCH_3OH/m^3,Bub#2	$8.89\mathrm{X}10^{2}$	$2.05\mathrm{X}10^{3}$	$4.52\mathrm{X}10^{4}$	$3.95\mathrm{X}10^{1}$	$1.75\mathrm{X}10^{3}$	$4.35\mathrm{X}10^{1}$
Total Conc. μgCH_3OH/m^3	1.20X104	$4.10\mathrm{X}10^{3}$	$7.99\mathrm{X}10^{5}$	$2.37\mathrm{X}10^{4}$	$4.55\mathrm{X}10^{4}$	$7.87\mathrm{X}10^{3}$
PPM Methanol	9.00	3.08	600	17.8	34.2	5.91
Std. Conc. μgCH_3OH/mℓ Bub.#1	78.4	0.784	784	7.84	78.4	7.84
Std. Area - Bubbler #1	10,000	500	20000	3000	15000	20000
Sample Area - Bubbler #1	2000	1500	2000	1000	3000	15000
Sam. Conc. μgC_2H_5OH/m^3Bub#1	$4.40\mathrm{X}10^{3}$	$2.03\mathrm{X}10^{3}$	$7.47\mathrm{X}10^{5}$	$2.6\mathrm{X}10^{3}$	$4.34\mathrm{X}10^{4}$	$1.94\mathrm{X}10^{3}$
Std. Conc. μgC_2H_5OH/mℓ Bub#2	7.84	0.784	7.84	0.784	7.84	0.784
Std. Area - Bubbler #2	15000	10000	5000	1000	2000	20000
Sample Area - Bubbler #2	5000	5000	4000	800	3000	1000
Sam. Conc. μgC_2H_5OH/m^3Bub#2	$7.23\mathrm{X}10^{2}$	$3.39\mathrm{X}10^{2}$	$2.99\mathrm{X}10^{4}$	$3.13\mathrm{X}10^{2}$	$1.30\mathrm{X}10^{4}$	$1.24\mathrm{X}10^{1}$
Total Conc. μgC_2H_5OH/m^3	$5.14\mathrm{X}10^{3}$	$2.37\mathrm{X}10^{3}$	$7.77\mathrm{X}10^{5}$	$2.92\mathrm{X}10^{3}$	$5.64\mathrm{X}10^{4}$	$1.95\mathrm{X}10^{3}$
PPM Ethanol	2.68	1.24	406	1.53	29.4	1.02

Figure 9. Methanol and ethanol sample collection sheet

The concentration from the two bubblers can be added for a total methanol concentration:

$$\text{Total } \mu g \text{ methanol/m}^3 = \text{conc.(Bubbler \#1)} + \text{conc.(Bubbler \#2)}$$
$$= 1.11 \times 10^4 \ \mu g/m^3 + 8.89 \times 10^2 \ \mu g/m^3$$
$$= 1.20 \times 10^4 \ \mu g/m^3$$

$$\text{PPM } CH_3OH = \mu g/m^3 \div \text{density } \mu g/m\ell$$

$$\text{density } \mu g/m\ell = \frac{\text{Mol. Wt. } (CH_3OH) \times 1000}{24.04\ell}$$

$$\text{Mol. Wt. } CH_3OH = 32.04 \text{ g/mole}$$

$$\text{density} = \frac{32.04 \times 1000}{24.04\ell} = 1333 \ \mu g/m\ell$$

$$\text{ppm methanol} = 1.20 \times 10^4 \div 1333 \ \mu g/m\ell = 9.00 \ m\ell/m^3 = 9.00 \text{ ppm}$$

The calculations for ethanol are carried out in the same manner by substituting the appropriate standard concentrations, peak areas and molecular weight into the above formulas. The calculations give the following concentrations.

Bubbler #1, 4.40×10^3 µg ethanol/m^3
Bubbler #2, 7.34×10^2 µg ethanol/m^3
Bubbler #1 and #2, 5.13×10^3 µg ethanol/m^3
ppm, 2.68 ethanol

Note: The values used in these calculations are picked from a range of temperatures, standards, dilution factors, etc., to validate the calculations and may not be representative of expected raw data. These calculations are presented to confirm that the manual and HP-67 calculations give the same results. This was confirmed on six sets of calculations.

LIST OF EQUIPMENT AND REAGENTS

The equipment and reagents for the analysis of the methanol and ethanol is divided into two groups. The first involves the sample acquisition and the second the instrumental analysis of the sample once it has been obtained. Manufacturer, stock number and any pertinent descriptive information are listed. The preparation of standards is also discussed.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.
2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.
3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.
4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.
5. Regulating valve, Nupro 4MG, stainless steel.
6. Teflon tubing, United States Plastics Corporation, 1/4" OD × 1/8" ID and 5/16" OD × 1/8" ID.
7. Teflon solenoid valve, the Fluorocarbon Company, Model DV2-144NCA1.
8. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.
9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.
10. Digital readout for dry gas meter.
11. Miscellaneous electrical switches, lights, wirings, etc.
12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.
13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.
14. 30 mℓ polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.
15. Deionized or distilled water.
16. Class A, 10 mℓ volumetric pipet.
17. Class A, 1000 mℓ volumetric flask.

Instrumental Analysis

1. 5 μl syringe, Hamilton Co., Reno, Nevada.
2. Perkin-Elmer Model 3920B gas chromatograph equipped with flame ionization detector.

3. Soltec Model B-281 1 mv recorder.

4. Hewlett-Packard Model 3353 gas chromatograph computer system with remote printer.

Preparation of Primary Standards

The primary standards for methanol, ethanol, and TBA are prepared by diluting a known volume of methanol, ethanol, or TBA with deionized (or distilled) water. Standards less than ∿500 ppm are prepared by diluting higher concentration standards with deionized water.

APPENDIX C

CALCULATION OF HYDROCARBON RECOVERY (IN GRAMS) FROM BAG PPMC

APPENDIX C

CALCULATION OF HYDROCARBON RECOVERY (In Grams) FROM BAG ppmC

$$\text{Bag ppmC}/10^6 \times \text{Purge flowrate, ft}^3/\text{min} \times \text{Purge time, min,}$$
$$\times \frac{\text{B.P., in Hg}}{29.92 \text{ in Hg}} \times \frac{528^\circ\text{F}}{^\circ\text{F} + 460} \times \frac{16.33 \text{ g}}{\text{ft}^3 \text{ HC}} = \text{Weight gasoline, g}$$

Example:

Bag concentration = 1520 ppmC

Purge flowrate = 1.53 ft^3/min

Purge time = 71.00 minutes

B.P. = 29.04 in Hg

Temp. = 82.4°F

$$1520/10^6 \times 1.53 \times 71.00 \times 29.04/29.92 \times 528/(82.4 + 460) \times 16.33 = 2.6 \text{ g HC}$$

If hydrocarbons are unleaded gasoline with density of 0.737 g/ml:

2.6 g x 1 ml/0.737 g = 3.5 ml gasoline

APPENDIX D

CHARCOAL WEIGHT LOSS AND CONTINUOUS HC LEVELS DURING THE THE PURGE CYCLE (OF DELCO IN-USE CHARCOAL) OF THE BUTANE WORKING CAPACITY PROCEDURE

APPENDIX D

CHARCOAL WEIGHT LOSS AND CONTINUOUS HC LEVELS DURING THE PURGE CYCLE (OF DELCO IN-USE CHARCOAL) OF THE BUTANE WORKING CAPACITY PROCEDURE

Cycle	Time, min	Continuous HC, ppmC	Weight Loss, g/hr
1	6.2	4500	—[a]
	12.1	2000	5.0
	22.8	810	2.4
	32.4	400	1.1
	34.5	300	—[b]
2	8.0	4400	45.8
	16.5	1400	3.9
	24.0	640	1.5
	32.0	320	0.7
	35.4	280	—[b]
3	7.0	3600	40.5
	14.0	1100	2.7
	21.0	640	1.2
	28.0	410	0.9
	31.2	300	—[b]
4	7.0	5000	36.2
	14.0	1900	5.1
	21.0	900	2.4
	28.0	460	1.0
	37.8	300	0.7
5	7.0	4900	46.4
	14.3	1600	4.5
	21.0	600	1.3
	28.0	390	0.8

---

[a] Canister not weighed before purge

[b] Canister gained weight slightly, probably due to water absorption during the weighing process.

APPENDIX E

WORKING CAPACITY FOR INDIVIDUAL WORKING CAPACITY CYCLES

APPENDIX E

WORKING CAPACITY FOR INDIVIDUAL WORKING CAPACITY CYCLES

Source	Canister Number	Working Capacity, g/50 g charcoal[a]			
		Cycle 1	Cycle 2	Cycle 3	Average
TVA	2090[a]	2.57	2.23	2.43	2.41
	2099[a]	1.96	2.09	2.70	2.79
	1925	1.95	2.43	2.19	2.19
	8887[a]	1.80	1.45	1.40	1.55
	1991[a]	2.24	2.29	2.02	2.18
	2067[a]	2.38	2.76	2.31	2.48
	1725	2.94	2.52	1.76	2.41
	1747	1.62	1.78	1.58	1.66
	8961[a]	1.46	1.23	1.42	1.37
	8902	1.34	1.85	1.46	1.55
SwRI (from DOE fleet)	201	1.72	2.35	2.15	2.07
	202	2.02	1.55	2.15	1.91
	205	2.34	1.65	2.03	2.01
	206	0.90	2.10	1.01	1.34
	101	--[b]	1.70	1.16	1.43
	102	1.65	1.81	1.86	1.77
	104	2.37	1.57	2.39	2.11
	106	1.97	2.25	1.48	1.90
EPA	A1480008	--[b]	1.28	1.01	1.15
	A1480049	1.80	1.33	1.48	1.54
	A1480073	1.62	1.82	1.82	1.75
	A1480039	1.81	1.37	2.29	1.82
	A1480060	1.51	2.58	2.58	2.22
	A1480096	1.16	1.97	2.06	1.73

---

[a] Working capacity = charcoal weight (when loaded to 1000 ppmC with butane) - charcoal weight (after cold purging to 600 ppmC hydrocarbons)

[b] No Data

APPENDIX F

SELECTED DETAILED HYDROCARBONS

APPENDIX F-1. SELECTED DETAILED HYDROCARBONS EMITTED DURING COLD AND HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE TVA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number											
	2090		2099		8887		1991		2067		8961	
	Cold[a]	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
1		--[b]	--	--	--	--	--	--	--	--	--	--
2		--	--	--	--	--	--	--	--	--	--	--
3		--	--	--	--	--	--	--	--	--	--	--
4		--	--	--	<0.01	0.29	--	0.62	--	0.03	--	--
5		--	--	--	--	--	--	--	--	--	--	--
6		--	--	--	--	--	--	--	--	--	--	--
7		--	--	--	0.05	--	--	--	--	--	0.02	--
8		--	--	--	--	--	--	--	--	--	<0.01	--
9		0.33	--	0.12	<0.01	<0.01	--	<0.01	--	0.11	0.01	0.02
10			--		0.03	--	--	--	--		0.01	
11			--		--	--	--	--	--		--	
12			--		0.01	--	--	--	--		0.01	
13			--		0.01	--	--	<0.01	--		0.01	
14			--		0.02	<0.01	--	--	--		0.02	
15			--		<0.01	<0.01	--	0.03	--		<0.01	
16			--		--	--	--	--	--		--	
17			<0.01		0.01	--	--	--	<0.01		0.01	
18						--	--	--				
19						--	--	--				
20			0.01		0.02	--	--	--	<0.01		0.01	
21			--		--	--	--	--	--		--	
22			<0.01		0.06	<0.01	--	--	<0.01		<0.01	
23							--	--				
24			0.01		0.03	<0.01	--	--	<0.01		0.05	
25			<0.01		0.01	--	--	<0.01	<0.01		0.02	
26						--	--					
27		<0.01	0.02		0.03	<0.01	<0.01	--	0.01		0.05	
28								--				
29		--	<0.01		0.01	--	--	--	<0.01		0.01	
30		--	<0.01		0.01	--	--	--	<0.01		0.01	
31		--				--	--	--				
32		--	<0.01		<0.01	--	--	--	<0.01		0.01	
33		--	0.01		0.02	<0.01	--	--	0.01		0.04	
34		--					--	--				
35		--	0.02	0.02	0.02	0.01	<0.01	0.03	0.01	0.03	0.04	0.02
36		--	0.01	--	0.01	<0.01	--	--	<0.01	--	0.03	--
37		--	0.02	--	0.02	0.01	<0.01	<0.01	0.01	<0.01	0.10	0.02
38		--		--								
39		--		--								
40		--		--		--		--		--		--
41		0.01	0.09	0.01	0.04	0.04	0.02	--	0.05	0.01	0.23	0.06
42								--				

---

[a] No data

[b] Not detected

APPENDIX F-1 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING COLD AND HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE TVA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number											
	2090		2099		8887		1991		2067		8961	
	Cold[a]	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
43		--[b]	--	--	--	--	--	--	--	--	--	--
44		--	--	--	--	--	--	--	--	--	--	--
45		0.01	0.04	--	0.02	0.02	0.01	--	0.02	0.01	0.10	0.03
46		0.03	0.08	0.01	0.06	0.11	0.04	--	0.06	0.03	0.19	0.15
47		0.02	0.04	0.02	0.02	0.02	0.02	--	0.02	0.01	0.10	0.06
48		--	0.01	<0.01	<0.01	<0.01	<0.01	--	<0.01	--	0.01	0.01
49		--						--		--		
50		--	0.03	--	0.01	0.01	0.01	--	0.01	--	0.06	0.02
51		--	0.01	<0.01	<0.01	<0.01	<0.01	--	<0.01	--	0.01	<0.01
52		0.03	0.03	0.04	0.01	0.05	0.03	0.02	0.02	0.03	0.06	0.09
53										--		
54		0.03	0.03	0.07	0.02	0.06	0.03	0.01	0.02	0.04	0.07	0.12
55		0.02	0.03	0.04	0.01	0.05	0.03	0.01	0.01	0.02	0.07	0.10
56		0.09	0.15	0.21	0.04	0.10	0.20	0.04	0.09	0.12	0.24	0.40
57												
58		0.04	0.03	0.09	0.01	0.08	0.04	0.01	0.02	0.06	0.08	0.17
59												
60												
61		0.04	0.03	0.08	0.01	0.07	0.04	0.01	0.01	0.04	0.07	0.14
62												
63		0.02	0.01	0.04	0.01	0.05	0.01	0.01	0.01	0.02	0.03	0.08
64		--	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01	0.01	0.02
65		--	0.01	0.03	<0.01	0.02	0.01	0.01	<0.01	0.01	0.01	0.05
66		0.03	0.01	0.06	0.01	0.06	0.03	0.02	0.01	0.04	0.04	0.13
67		0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.03
68		0.01	<0.01	0.02	<0.01	0.02	0.01	0.01	<0.01	0.01	0.01	0.03
69		0.04	0.01	0.06	<0.01	0.06	0.01	0.03	<0.01	0.05	0.02	0.11
70												
71		0.10	0.02	0.17	0.01	0.06	0.05	0.10	0.01	0.12	0.03	0.15
72		--	<0.01	--	<0.01	0.03	0.01	0.02	<0.01	0.03	0.01	0.05
73		0.62	0.09	0.79	0.04	0.27	0.19	0.52	0.06	0.68	0.12	0.64
74												
75		--	0.01	0.12	0.01	0.11		0.07	0.01	0.16	0.02	0.19
76		--										
77		0.11	0.01	0.13	0.01	0.11	0.02	0.08	0.01	0.16	0.03	0.20
78		0.35	0.04	0.48	0.02	0.15	0.08	0.39	0.03	0.47	0.05	0.31
79		0.14	0.01	0.12	0.01	0.08	0.01	0.10	0.01	0.22	0.02	0.16
80		0.04	<0.01	0.04	<0.01	0.02	<0.01	0.03	<0.01	0.05	<0.01	0.03
81		0.27	0.02	0.21	0.01	0.05	0.02	0.23	0.02	0.38	0.02	0.11
82		1.19	0.07	0.86	0.05	0.21	0.08	1.06	0.08	1.63	0.10	0.52
83		0.67	0.02	0.43	0.02	0.09	0.03	0.55	0.04	0.86	0.03	0.17

---

[a] No data

[b] Not detected

APPENDIX F-1 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING COLD AND HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE TVA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number											
	2090		2099		8887		1991		2067		8961	
	Cold[a]	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
85		0.38	0.01	0.21	0.01	0.03	0.01	0.27	--[b]	0.45	0.01	0.06
86												
87		0.42	0.02	0.28	0.02	0.04	0.02	0.43	0.03	0.54	0.03	0.07
88		0.18	0.01	0.13	0.01	0.02	0.01	0.26	0.01	0.34	0.01	0.03
89		0.17	<0.01	0.10	<0.01	0.01	<0.01	0.14	0.01	0.17	<0.01	0.01
90		0.22	0.008	0.13	0.01	0.02	0.01	0.16	0.02	0.23	0.01	0.02
91		0.30	0.013	0.18	0.01	0.03	0.01	0.24	0.02	0.34	0.02	0.04
92		0.27	0.011	0.16	0.01	0.02	0.01	0.21	0.02	0.31	0.06	0.04
93												
94		0.47	0.018	0.28	0.02	0.04	0.01	0.33	0.04	0.49	0.03	0.06
95		0.20	<0.01	0.12	<0.01	0.01	<0.01	0.11	0.01	0.17	0.01	0.01
96		0.41	0.02	0.27	0.02	0.03	0.01	0.31	0.03	0.43	0.03	0.05
97		0.13	--	--	<0.01	0.01	<0.01	0.08	<0.01	0.11	0.01	0.01
98		0.01	--	--	--	<0.01	--	0.04	--	0.03	<0.01	0.01
99			--	--	--		--		--			
Total		7.41	1.14	6.14	0.93	2.58	2.02	6.60	0.85	9.06	2.53	4.80

---

[a] No data

[b] Not detected

APPENDIX F-2. SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE TVA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number									
	2090	2099	1925	8887	1991	2067	1725	1747	8961	8902
1	--[a]	--	--	--	--	--	--	--	--	--
2	--	--	--	--	--	--	--	--	--	--
3	--	--	0.01	--	--	--	0.02	0.03	--	--
4	--	--	0.16	0.29	0.62	0.03	0.05	0.02	--	0.02
5	--	--	--	--	--	--	--	--	--	--
6	--	--	--	--	--	--	--	--	--	--
7	--	--		--	--	--	--	--	--	<0.01
8	--	--	0.13	--	--	--	--	--	--	<0.01
9	0.33	0.12		<0.01	<0.01	0.11	--	0.01	0.02	<0.01
10				--	--		--	--		--
11				--	--		0.02	--		--
12				--	--		0.02	--		--
13				--	<0.01		0.05	0.01		<0.01
14				<0.01	--		0.02	--		--
15				<0.01	0.03		0.03	0.03		0.01
16			--	--	--		--	--		--
17			--	--	--		--	--		--
18			--	--	--		--	--		--
19			--	--	--		--	--		--
20			<0.01	--	--		<0.01	--		<0.01
21			--	--	--		--	--		--
22			--	<0.01	--		0.01	--		0.01
23			--		--			--		
24			0.01	<0.01	--		0.02	--		<0.01
25			--	--	<0.01		--	--		<0.01
26			--	--			--	--		
27	<0.01		0.03	<0.01	--		0.04	0.03		0.01
28					--					
29	--		--	--	--		--	--		--
30	--		--	--	--		--	--		--
31	--		--	--	--		--	--		--
32	--		--	--	--		--	--		--
33	--		--		--			--		
34	--		--	<0.01	--		0.01	--		<0.01
35	--	0.02	0.01	0.01	0.03	0.03	0.01	0.04	0.02	0.01
36	--	--	--	<0.01	--	--	0.01	--	--	<0.01
37	--	--	0.03	0.01	<0.01	<0.01	0.03	0.01	0.02	0.01
38	--	--								
39	--	--								
40	--	--	--	--	--	--	--	--	--	--
41	0.01	0.01	0.01	0.04	--	0.01	--	--	0.06	0.08
42					--		--	--		

---

[a]-- Not detected

APPENDIX F-2 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE TVA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number 2090	2099	1925	8887	1991	2067	1725	1747	8961	8902
43	--[a]	--	--	--	--	--	--	--	--	--
44	--	--	--	--	--	--	--	--	--	--
45	0.01	--	<0.01	0.02	--	0.01	--	--	0.03	0.04
46	0.03	0.01	0.03	0.11	--	0.03	--	0.03	0.15	0.21
47	0.02	0.02	0.04	0.02	--	0.01	0.04	0.01	0.06	0.05
48	--	<0.01	--	<0.01	--	--	--	--	0.01	<0.01
49	--		--		--	--	--	--		
50	--	--	--	0.01	--	--	--	--	0.02	0.01
51	--	<0.01	--	<0.01	--	--	--	--	<0.01	<0.01
52	0.03	0.04	0.01	0.05	0.02	0.03	0.04	0.04	0.09	0.10
53										
54	0.03	0.07	0.03	0.06	<0.01	0.04	0.07	0.08	0.12	0.10
55	0.02	0.04	0.02	0.05	0.01	0.02	0.05	0.09	0.10	0.08
56	0.09	0.21	0.09	0.10	0.04	0.12	0.21	0.20	0.40	0.09
57			--							0.06
58	0.04	0.09	0.03	0.08	0.01	0.06	0.07	0.06	0.17	0.18
59										
60										
61	0.04	0.08	0.02	0.07	0.01	0.04	0.06	0.05	0.14	0.14
62										
63	0.02	0.04	0.02	0.05	0.01	0.02	0.05	0.10	0.08	0.14
64	--	<0.01	<0.01	0.01	0.01	0.01	0.01	<0.01	0.02	0.01
65	--	0.03	0.02	0.02	0.01	0.01	0.03	0.01	0.05	0.03
66	0.03	0.06	0.03	0.06	0.02	0.04	0.06	0.07	0.13	0.17
67	0.01	0.01	<0.01	0.01	<0.01	0.01	0.01	0.03	0.03	0.05
68	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.03	0.05
69	0.04	0.06	0.02	0.06	0.03	0.05	0.04	0.07	0.11	0.15
70										
71	0.10	0.17	0.09	0.06	0.10	0.12	0.14	0.30	0.15	0.09
72	--	--	0.01	0.03	0.02	0.03	0.02	0.04	0.05	0.07
73	0.62	0.79	0.41	0.27	0.52	0.68	0.61	1.64	0.64	0.40
74										
75	--	0.12	0.05	0.11	0.07	0.16	0.08		0.19	0.32
76	--									
77	0.11	0.13	0.05	0.11	0.08	0.16	0.08	0.18	0.20	0.25
78	0.35	0.48	0.26	0.15	0.39	0.47	0.35	0.90	0.31	0.26
79	0.14	0.12	0.05	0.08	0.10	0.22	0.08	0.21	0.16	0.18
80	0.04	0.04	0.02	0.02	0.03	0.05	0.02	0.04	0.03	0.03
81	0.27	0.21	0.13	0.05	0.23	0.38	0.14	0.39	0.11	0.11
82	1.19	0.86	0.55	0.21	1.06	1.63	0.60	1.77	0.52	0.40
83	0.67	0.43	0.30	0.09	0.55	0.86	0.30	0.84	0.17	0.19
84	1.57	1.05	0.97	0.22	1.65	2.11	0.83	2.45	0.34	0.35

---

[a] -- Not detected

APPENDIX F-2 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE TVA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number									
	2090	2099	1925	8887	1991	2067	1725	1747	8961	8902
85	0.38	0.21	0.17	0.03	0.27	0.45	0.16	0.41	0.06	0.07
86										
87	0.42	0.28	0.29	0.04	0.43	0.54	0.21	0.56	0.07	0.07
88	0.18	0.13	0.11	0.02	0.26	0.34	0.08	0.33	0.03	0.01
89	0.17	0.10	0.08	0.01	0.14	0.17	0.07	--[a]	0.01	0.01
90	0.22	0.13	0.12	0.02	0.16	0.23	0.09	0.21	0.02	0.02
91	0.30	0.18	0.20	0.03	0.24	0.34	0.13	0.34	0.04	0.03
92	0.27	0.16	0.19	0.02	0.21	0.31	0.12	0.30	0.04	--
93										--
94	0.47	0.28	0.31	0.04	0.33	0.49	0.20	0.48	0.06	--
95	0.20	0.12	0.12	0.01	0.11	0.17	0.08	0.16	0.01	--
96	0.41	0.27	0.33	0.03	0.31	0.43	0.19	0.45	0.05	--
97	0.13	--	0.14	0.01	0.08	0.11	0.06	0.13	0.01	--
98	0.01	--	0.17	<0.01	0.04	0.03	0.02	0.12	<0.01	--
99		--								--
Total	8.99	7.22	5.92	2.92	8.30	11.18	5.76	13.30	5.15	4.78

---

[a]-- Not detected

APPENDIX F-3. SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE SWRI EVAPORATIVE CANISTERS (DOE FLEET), g

Compound Number	Canister Number							
	201	202	205	206	101	102	104	106[a]
1	--[b]	--	--	--	--	--	--	
2	--	--	--	--	--	--	--	
3	--	--	--	--	--	--	--	
4	0.03	0.03	0.04	0.02	0.03	0.02	--	
5	--	--	--	--	--	--	--	
6	--	--	--	--	--	--	--	
7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
8	--	<0.01	--	<0.01	<0.01	--	<0.01	
9	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	
10	--	--		--	--	--	--	
11	--	--	<0.01	--	--	--	--	
12	--	--	<0.01	--	--	--	--	
13	--	--	<0.01	--	--	--	--	
14	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
16	--	--	--	--	--	--	--	
17	--	--	--	--	--	--	--	
18	--	--	--	--	--	--	--	
19	--	--	--	--	--	--	--	
20	<0.01	<0.01	0.01	0.01	<0.01	<0.01	--	
21	--	--	--	--	--	--	--	
22	<0.01	0.02	0.03	0.05	0.01	0.11	<0.01	
23								
24	<0.01	0.02	0.02	0.04	<0.01	0.01	<0.01	
25	<0.01	--	--	--	--	--	--	
26		--	--	--	--	--	--	
27	0.02	0.05	0.04	0.09	0.01	0.04	<0.01	
28								
29	--	--	--	--	--	--	--	
30	--	--	--	--	--	--	--	
31	--	--	--	--	--	--	--	
32	--	--	--	--	--	--	--	
33	<0.01	0.01	0.02	0.02	0.01	0.01	<0.01	
34								
35	0.01	0.02	0.03	0.04	0.01	0.02	0.01	
36	--	--	--	--	<0.01	<0.01	--	
37	0.01	0.03	0.02	0.04	0.01	0.02	--	
38							--	
39							--	
40	--	--	--	--	--	--	--	
41	0.14	0.24	0.14	0.35	0.15	0.19	--	
42							--	

---

[a] Hole in sample bag, no data

[b] -- Not detected

APPENDIX F-3 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE SWRI EVAPORATIVE CANISTERS (DOE FLEET), g

Compound Number	Canister Number							
	201	202	205	206	101	102	104	106[a]
43	--[b]	--	--	--	--	--	--	
44	--	--	--	--	--	--	--	
45	0.12	0.22	0.12	0.29	0.14	0.17	0.09	
46	0.25	0.33	0.19	0.48	0.25	0.24	0.12	
47	0.21	0.28	0.14	0.34	0.23	0.23	0.14	
48	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01	
49								
50	0.01	0.02	0.02	0.03	0.01	0.02	0.01	
51	<0.01	0.01	--	0.01	<0.01	<0.01	<0.01	
52	0.28	0.30	0.14	0.29	0.11	0.23	0.12	
53								
54	0.19	0.19	0.09	0.19	0.18	0.18	0.10	
55	0.19	0.19	0.09	0.19	0.20	0.21	0.12	
56	0.53	0.68	0.39	0.51	0.55	0.59	0.54	
57								
58								
59	0.52	0.52	0.24	0.35	0.36	0.40	0.21	
60								
61	0.42	0.42	0.20	0.30	0.30	0.36	0.19	
62								
63	0.26	0.23	0.14	0.13	0.17	0.20	0.09	
64	0.03	--	--	--	--	--	--	
65	0.03	--	--	--	--	--	--	
66	0.33	0.30	0.17	0.16	0.22	0.28	0.14	
67	0.05	0.67	0.03	0.02	0.04	0.05	0.02	
68	0.06	0.05	0.05	0.02	0.04	0.06	0.03	
69	0.15	0.12	0.12	0.05	0.09	0.13	0.06	
70								
71	0.13	0.10	0.07	0.07	0.14	0.11	0.13	
72	0.05	0.02	0.05	0.01	0.02	0.05	0.02	
73	0.75	0.42	0.29	0.31	0.68	0.47	0.72	
74								
75		0.13	0.26	0.04	0.10	0.15		
76								
77	0.17	0.12	0.19	0.05	0.13	0.16	0.09	
78	0.24	0.15	0.16	0.13	0.27	0.19	0.31	
79	0.09	0.06	0.14	0.03	0.08	0.09	0.06	
80	0.01	0.01	0.01	<0.01	0.01	0.01	<0.01	
81	0.07	0.04	0.12	0.03	0.09	0.07	0.08	
82	0.30	0.21	0.62	0.17	0.38	0.34	0.44	
83	0.08	0.06	0.21	0.06	0.10	0.09	0.14	

---

[a] Hole in sample bag, no data

[b] -- Not detected

APPENDIX F-3 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE SWRI EVAPORATIVE CANISTERS (DOE FLEET), g

Compound Number	Canister Number							
	201	202	205	206	101	102	104	106[a]
84	0.20	0.19	0.80	0.20	0.25	--[b]	0.54	
85	0.02	0.02	0.07	0.03	0.03	0.29	0.04	
86								
87	0.03	0.01	0.16	0.06	0.04	0.04	0.12	
88	0.01	0.02	0.06	0.02	0.02	0.02	0.05	
89	<0.01	<0.01	0.01	0.01	0.01	<0.01	0.01	
90	0.01	0.02	0.08	0.02	0.02	0.03	0.04	
91	0.01	0.03	0.10	0.03	0.02	0.02	0.06	
92	0.01	0.02	0.10	0.03	0.02	0.02	0.06	
93								
94	0.03	0.03	0.15	0.05	0.03	0.05	0.09	
95	--	0.01	0.01	0.01	0.01	0.01	0.02	
96	0.02	0.03	0.14	0.05	0.03	0.03	0.09	
97	--	0.01	<0.01	0.01	--	<0.01	0.01	
98	--	--			--	--		
99	--	--	0.02	<0.01	--	--	0.02	
Total	6.19	6.74	6.39	5.51	5.70	6.11	5.25	

---

[a] Hole in sample bag, no data

[b] -- Not detected

APPENDIX F-4. SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE EPA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number (A148-)					
	0008	0049	0073	0039	0060	0096
1	--[a]	--	--	--	--	--
2	--	--	--	--	--	--
3	--	--	--	--	--	0.01
4	0.03	--	--	--	--	0.02
5	--	--	--	--	--	--
6	--	--	--	--	--	--
7	<0.01	<0.01	0.02		0.02	--
8	<0.01	<0.01		2.33		--
9	<0.01	<0.01				<0.01
10	<0.01	--				--
11	--	--				--
12	--	--				--
13	<0.01	<0.01				--
14	<0.01	<0.01				<0.01
15	<0.01	<0.01				<0.01
16	--	--	--		--	--
17	--	--	--		--	--
18	--	--	--		--	--
19	--	--	--		--	--
20	0.01	<0.01	0.01		0.01	--
21	--	--	--	--	--	--
22	0.03	0.01	0.02	0.01	0.03	<0.01
23						
24	0.02	0.01	0.02	<0.01	0.02	<0.01
25	<0.01	--	<0.01	--	<0.01	--
26		--		--		--
27	0.04	0.01	0.04	0.01	0.04	0.01
28						
29	<0.01	--	<0.01	--	--	--
30	<0.01	--	<0.01	--	--	--
31		--		--	--	--
32	<0.01	--	<0.01	--	--	--
33	0.01	0.01	0.01	--	0.01	<0.01
34				--		
35	0.10	0.03	0.08	0.02	0.07	0.03
36	<0.01	<0.01	<0.01	--	--	<0.01
37	0.04	0.01	0.01	0.02	0.03	0.02
38						
39						
40	--	--	--	--	--	--
41	0.50	0.18	0.39	0.19	0.31	0.15
42	--					

---

[a] -- Not detected

APPENDIX F-4 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE EPA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number (A148-)					
	0008	0049	0073	0039	0060	0096
43	--[a]	--	--	--	--	--
44	--	--	--	--	--	--
45	0.23	0.12	0.26	0.08	0.17	0.08
46	1.14	0.26	0.54	0.17	0.68	0.82
47	0.23	0.13	0.22	0.12	0.18	0.15
48	0.01	0.01	0.01	--	0.01	0.01
49				--		
50	0.03	0.02	0.05	0.01	0.02	0.02
51	0.01	0.01	0.02	0.01	0.01	0.01
52	0.25	0.17	0.24	0.08	0.17	0.20
53						
54	0.28	0.17	0.22	0.09	0.16	0.24
55	0.19	0.20	0.22	0.07	0.14	0.24
56	0.40	0.62	0.76	0.20	0.34	0.49
57						
58	0.22	0.24	0.32	0.09	0.18	0.19
59						
60						
61	0.19	0.22	0.29	0.07	0.16	0.15
62						
63	0.05	0.08	0.08	0.03	0.06	0.12
64	0.01	0.03	0.04	--	0.02	0.01
65	0.01	<0.01	0.03	--	0.02	0.01
66	0.09	0.13	0.14	0.02	0.10	0.10
67	0.01	0.02	0.02	0.01	0.01	0.02
68	0.01	0.02	0.03	0.01	0.02	0.02
69	0.03	0.06	0.07	0.06	0.05	0.06
70						
71	0.08	0.16	0.15	0.04	0.10	0.08
72	0.01	0.02	0.02	0.02	0.02	0.02
73	0.27	0.72	0.62	0.18	0.44	0.36
74						
75	0.03			0.03	0.08	0.09
76						
77	0.04	0.08	0.07	0.03	0.09	0.09
78	0.11	0.28	0.21	0.09	0.20	0.18
79	0.02	0.04	0.03	0.02	0.06	0.07
80	<0.01	0.01	0.01	<0.01	0.01	0.01
81	0.02	0.05	0.04	0.17	0.06	0.07
82	0.11	0.24	0.12	--	0.30	0.32
83	0.04	0.07	0.08	0.19	0.10	0.14
84	0.11	0.24	0.17	0.13	0.35	0.44

---

[a]-- Not detected

APPENDIX F-4 (CONT'D). SELECTED DETAILED HYDROCARBONS EMITTED DURING HOT PURGING OF 50 g SAMPLES OF CHARCOAL FROM IN-USE EPA EVAPORATIVE CANISTERS, g

Compound Number	Canister Number (A148-)					
	0008	0049	0073	0039	0060	0096
85	0.02	0.02	0.01	0.02	0.04	0.07
86						
87	0.02	0.05	0.03	0.02	0.08	0.11
88	0.01	0.02	0.01	0.01	0.03	0.05
89	<0.01	<0.01	<0.01	--[a]	0.01	0.02
90	<0.01	0.01	0.01	0.05	0.02	0.04
91	0.02	0.02	0.02	0.02	0.05	0.07
92	0.01	0.02	0.01	0.04	0.04	0.06
93						
94	0.02	0.03	0.02	--	0.07	0.10
95	<0.01	<0.01	<0.01	--	--	0.02
96	--	0.03	0.02	0.04	0.06	0.09
97	--	<0.01	<0.01	--	0.01	0.02
98	--	--	--	--		
99	--	--	--	--	0.01	0.02
Total	5.28	5.00	5.89	4.82	5.28	5.79

---

[a] Not detected

APPENDIX F-5. PERCENTAGE OF DETAILED HYDROCARBONS PURGED FROM 50 g CHARCOAL SAMPLES FROM IN-USE TVA GASOLINE EVAPORATIVE CANISTERS[a]

	Canister Number								
	2090			2099			8887		
Compound Number	Cold Purge[b]	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge
4		98	--[c]	--	98	9[d]	—	94	8[d]
7		--	--	--	--	--	4	--	--
10		--	--	--	--	--	2	--	--
12		--	--	--	--	--	1	--	--
13		--	--	--	--	--	1	--	--
14		--	--	--	--	--	1	--	--
20		--	--	1	--	--	1	--	--
21		--	--	--	--	1	--	--	--
22,23		--	--	--	--	--	5	--	--
24		--	--	1	--	--	3	--	--
25,26		--	--	--	--	--	1	--	--
27,28		--	--	1	--	--	2	--	--
29		--	--	--	--	--	1	--	--
30,31		--	--	--	--	--	1	--	--
33,34		--	--	1	--	--	2	--	--
35		--	--	1	--	--	1	--	--
36		--	--	--	--	--	1	--	--
37,38,39,40		--	--	2	--	--	1	--	--
41,42		--	--	6	--	--	4	--	1
45		--	--	3	--	--	2	--	1
46		--	--	6	--	--	5	--	3
47		--	--	3	--	--	1	--	1
50		--	--	2	--	--	1	--	--
52,53		--	--	2	--	--	1	--	1
54		--	--	2	--	1	1	--	2
55		--	--	2	--	--	1	--	1
56,57		--	1	10	--	2	3	--	3
58,59,60		--	--	2	--	1	1	--	2

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] No data

[c] -- is less than 1

[d] Butane peak not added into totals, probably a residue from the previous working capacity analysis.

APPENDIX F-5 (CONT'D). PERCENTAGE OF DETAILED HYDROCARBONS PURGED FROM 50 g CHARCOAL SAMPLES FROM IN-USE TVA GASOLINE EVAPORATIVE CANISTERS[a]

	Canister Number								
	2090			2099			8887		
Compound Number	Cold Purge[b]	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge
61,62		--[c]	--	2	--	1	1	--	2
63		--	--	1	--	--	1	--	1
65		--	--	1	--	--	--	--	--
66		--	--	1	--	1	1	--	2
69,70		--	--	--	--	1	--	--	2
71		--	1	2	--	1	1	--	2
72		--	--	--	--	--	--	--	1
73,74		--	4	6	--	7	3	--	7
75,76		--	--	1	--	1	1	--	3
77		--	1	1	--	1	1	--	3
78		--	2	3	--	4	2	--	4
79		--	1	1	--	1	1	--	2
81		--	2	1	--	2	1	--	1
82		--	8	4	--	7	4	--	6
83		--	5	2	--	4	2	--	2
84		--	11	5	--	9	6	--	6
85,86		--	3	1	--	2	--	--	1
87		--	3	1	--	2	1	--	1
88		--	1	1	--	1	1	--	--
89		--	1	--	--	1	--	--	--
90		--	2	1	--	1	1	--	--
91		--	2	1	--	2	1	--	1
92,93		--	2	1	--	1	1	--	1
94		--	3	1	--	2	2	--	1
95		--	1	--	--	1	--	--	--
96		--	3	1	--	2	2	--	1
97		--	1	--	--	--	--	--	--

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] No data

[c] -- is less than 1

[d] Butane peak not added into totals, probably a residue from the previous working capacity analysis.

APPENDIX F-6. PERCENTAGE OF DETAILED HYDROCARBONS PURGED FROM 50 g CHARCOAL SAMPLES FROM IN-USE TVA BLEND EVAPORATIVE CANISTERS[a]

	Canister Number								
	1991			2067			8961		
Compound Number	Cold Purge	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge
4	--[b]	97	5[c]	--	99	--	--	86	--
7	--	--	--	--	--	--	1	--	--
14	--	--	--	--	--	--	1	--	--
24	--	--	--	--	--	--	1	--	--
27,28	--	--	--	--	--	--	2	--	--
33,34	--	--	--	--	--	--	1	--	--
35	--	--	--	1	--	--	1	--	--
36	--	--	--	--	--	--	1	--	--
37,38,39,40	--	--	--	1	--	--	3	--	--
41,42	1	--	--	4	--	--	7	--	1
45	1	--	--	2	--	--	3	--	--
46	3	--	--	4	--	--	6	1	2
47	1	--	--	2	--	--	3	--	1
50	1	--	--	1	--	--	2	--	--
52,53	2	--	--	1	--	--	2	--	1
54	2	--	--	1	--	--	2	--	2
55	2	--	--	1	--	--	2	--	1
56,57	14	--	--	6	--	1	7	1	5
58,59,60	3	--	--	1	--	--	2	--	2
61,62	2	--	--	1	--	--	2	--	2
63	1	--	--	--	--	--	1	--	1
65	1	--	--	--	--	--	--	--	1
66	2	--	--	1	--	--	1	--	2

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] -- is less than 1

[c] Butane peak not added into totals, probably a residue from the previous working capacity analysis.

APPENDIX F-6 (CONT'D). PERCENTAGE OF DETAILED HYDROCARBONS PURGED FROM 50 g CHARCOAL SAMPLES FROM IN-USE TVA BLEND EVAPORATIVE CANISTERS[a]

	Canister Number								
	1991			2067			8961		
Compound Number	Cold Purge	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge	Cold Purge	Working Capacity Purge	Hot Purge
69,70	1	--[b]	--	--	--	--	1	--	1
71	3	--	1	1	--	1	1	--	2
72	--	--	--	--	--	--	--	--	1
73,74	13	--	4	4	--	4	4	1	8
75,76		--	1	1	--	1	1	--	3
77	1	--	1	1	--	1	1	--	3
78	5	--	3	2	--	3	2	--	4
79	1	--	1	1	--	1	1	--	2
81	1	--	2	1	--	2	1	--	1
82	6	--	9	6	--	10	3	--	7
83	2	--	5	3	--	5	1	--	2
84	6	--	14	8	--	13	4	--	4
85,86	1	--	2	--	--	3	--	--	1
87	1	--	4	2	--	3	1	--	1
88	1	--	2	1	--	2	--	--	--
89	--	--	1	1	--	1	--	--	--
90	--	--	1	1	--	1	--	--	--
91	1	--	2	2	--	2	1	--	1
92,93	1	--	2	2	--	2	2	--	--
94	1	--	3	3	--	3	1	--	1
95	--	--	1	1	--	1	--	--	--
96	1	--	3	2	--	3	1	--	1
97	--	--	1	--	--	1	--	--	--

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] -- is less than 1

[c] Butane peak not added into totals, probably a residue from the previous working capacity analysis.

APPENDIX F-7. PERCENTAGE OF DETAILED HYDROCARBONS HOT PURGED FROM 50 g CHARCOAL SAMPLES FROM IN-USE TVA EVAPORATIVE CANISTERS[a]

Compound Number	Canister Number 1925	1725	1747	8902
4	2[b]	1[b]	--[c]	--
13	--	1	--	--
41,42	--	--	--	1
45	--	--	--	1
46	--	--	--	3
47	--	--	--	1
52,53	--	1	--	2
54	--	1	--	2
55	--	1	--	1
56,57	1	3	1	1
58,59,60	--	1	--	3
61,62	--	1	--	2
63	--	1	1	2
66	--	1	--	3
67	--	--	--	1
68	--	--	--	1
69,70	--	1	--	2
71	1	2	2	1
72	--	--	--	1
73,74	4	7	9	6
75,76	1	1		5
77	1	1	1	4
78	3	4	5	4
79	1	1	1	3
80	--	--	--	1
81	1	2	2	2
82	6	7	9	6
83	3	4	4	3
84	11	10	13	5
85,86	2	2	2	1
87	3	3	3	1
88	1	1	2	1
89	1	1	--	--
90	1	1	1	--
91	2	2	2	1
92,93	2	2	2	--
94	3	2	3	--
95	1	1	1	--
96	4	2	2	--
97	1	1	1	--
98,99	2	--	1	--

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] Butane peak not added into totals, probably a residue from the previous working capacity analysis.

[c] -- is less than 1

APPENDIX F-8 PERCENTAGE OF DETAILED HYDROCARBONS IN HOT PURGED CHARCOAL EFFLUENT FROM 50 g SAMPLES FROM IN-USE SWRI EVAPORATIVE CANISTERS (DOE FLEET)[a]

Compound Number	Canister Number							
	201	202	205	206	101	102	104	106
20	--[b]	--	--	1	--	--	--	ND[c]
22,23	--	--	--	1	--	--	--	ND
24	--	--	--	1	--	--	--	ND
27,28	--	--	1	2	--	--	--	ND
35	--	--	--	1	--	--	--	ND
37,38,39	--	--	--	1	--	--	--	ND
41,42	2	3	2	6	2	3	--	ND
45	2	3	1	5	2	2	2	ND
46	4	5	2	8	4	4	2	ND
47	3	4	2	5	3	3	2	ND
52,53	4	4	2	5	2	3	2	ND
54	3	3	1	3	3	3	2	ND
55	3	3	1	3	3	3	2	ND
56,57	8	10	5	8	8	9	9	ND
58,59,60	7	7	3	6	5	6	3	ND
61,62	6	6	3	5	5	5	3	ND
63	4	3	2	2	3	3	1	ND
66	5	4	2	3	3	4	2	ND
67	1	1	--	--	1	1	--	ND
68	1	1	--	--	1	1	--	ND
69,70	2	2	1	1	1	2	1	ND
71	2	1	1	1	2	2	2	ND
72	1	--	1	--	--	1	--	ND
73,74	11	6	4	5	10	7	12	ND
75,76		2	3	1	1	1		ND
77	2	2	2	1	2	2	1	ND
78	3	2	2	2	4	3	5	ND
79	1	1	2	--	1	1	1	ND
81	1	1	2	1	1	1	1	ND
82	4	3	8	3	6	5	7	ND
83	1	1	3	1	2	1	2	ND
84	3	3	10	3	4	--	9	ND
85,86	--	--	1	1	--	4	1	ND
87	--	--	2	1	1	1	2	ND
88	--	--	1	--	--	--	1	ND
90	--	--	1	--	--	--	1	ND
91	--	--	1	--	--	--	1	ND
92,93	--	--	1	--	--	--	1	ND
94	--	1	2	1	--	--	2	ND
96	--	--	2	1	--	--	1	ND

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] -- is less than 1

[c] ND - No Data

APPENDIX F-9. PERCENTAGE OF DETAILED HYDROCARBONS IN HOT PURGED CHARCOAL EFFLUENT FROM 50 g SAMPLES FROM IN-USE EPA EVAPORATIVE CANISTERS[a]

Compound Number	Canister Number (A148-)					
	0008	0049	0073	0039	0060	0096
22,23	--[b]	--	--	--	1	--
27,28	1	--	1	--	1	--
35	2	1	1	--	--	--
37,38,39	1	--	--	--	--	--
40,41,42	9	3	6	3	5	2
45	4	2	4	1	3	1
46	21	5	8	3	11	12
47	4	2	3	2	3	2
50	--	--	1	--	--	--
52,53	5	3	4	1	3	3
54	5	3	3	1	3	4
55	3	4	3	1	2	4
56,57	7	11	12	3	5	7
58,59,60	4	4	5	2	3	3
61,62	3	4	4	1	3	2
63	1	1	1	1	1	2
64	--	--	1	--	--	--
65	--	--	1	--	--	--
66	2	2	2	--	2	2
69,70	1	1	1	1	1	1
71	2	3	2	1	2	1
73,74	5	13	10	3	7	5
75,76	1			1	1	1
77	1	1	1	1	1	1
78	2	5	3	2	3	3
79	--	1	1	--	1	1
81	--	1	1	3	1	1
82	2	4	2	1	5	5
83	1	1	1	3	2	2
84	2	4	3	2	6	6
85,86	--	--	--	--	1	1
87	--	1	1	--	1	2
88	--	--	--	--	--	1
90	--	--	--	1	--	1
91	--	--	--	--	1	1
92,93	--	--	--	1	1	1
94	--	1	--	--	1	1
96	--	1	--	--	1	1

---

[a] Percentages were calculated based on the peak area of individual (or groups of inseparable) compounds as a fraction of total area.

[b] -- is less than 1

APPENDIX G

PERCENTAGE OF PARAFFINS, OLEFINS, AND AROMATICS

APPENDIX G-1. PERCENTAGE OF PARAFFINS, OLEFINS, AND AROMATICS IN PURGED CHARCOAL EFFLUENT FROM 50 g SAMPLES FROM IN-USE EVAPORATIVE CANISTERS[a]

Canister Identification	Purge Cycle	Paraffins	Olefins	Aromatics
TVA 2090	cold	--[b]	--	--
2099	cold	55	6	39
8887	cold	48	17	35
1991	cold	60	3	37
2067	cold	44	2	54
8961	cold	61	8	31
	Avg .	53	7	39
TVA 2090	hot	22	0	78
2099	hot	36	2	62
1925	hot	24	0	76
8887	hot	58	0	42
1991	hot	29	0	71
2067	hot	25	0	75
1725	hot	30	2	68
1747	hot	25	0	75
8961	hot	52	2	46
8902	hot	61	2	38
	Avg .	36	1	63
DOE 201	hot	81	0	19
202	hot	75	0	25
205	hot	50	0	50
206	hot	75	0	25
101	hot	61	0	39
102	hot	74	0	26
104	hot	47	0	53
106	hot	--	--	--
	Avg .	66	0	34
EPA A148-				
0008	hot	81	0	19
0049	hot	65	0	35
0073	hot	71	6	23
0039	hot	47	0	53
0060	hot	60	0	40
0096	hot	61	0	39
	Avg .	64	1	35

---

[a] Percentages were calculated based on peak areas of paraffins, olefins, and aromatics as a fraction of the sum of the group area.

[b] No data